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On the corrosion risk presented by chloride bound in concrete

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Abstract

In previous work the influence of the solid phases of cement hydration on the pore solution chemistry during corrosion initiation has been discussed. It was noted that, because a fall in local pH is necessary for stable pits to develop on the passive steel, much of the chloride bound in concrete may participate in the process of corrosion initiation. At least two phases in hydrated ordinary Portland cement (OPC) will release such bound chloride before the pH falls to 11. In this work, these studies have been extended to include OPC blended with 10% calcium aluminate cement (CAC) and sulphate resisting Portland cement (SRPC). Evidence of a third phase that releases bound chloride was uncovered. Once again the data confirms that most of the bound chloride will be released by a relatively small reduction in pH. The release of chloride at such a high pH value compared to that required to sustain passive film breakdown suggests that the corrosion risk presented by bound chloride may be very similar to that presented by free chloride in concrete. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Concrete; Corrosion; Chloride threshold; Passive steel; Bound chloride

1. Introduction

The corrosion of steel in concrete induced by chloride ion contamination is a major problem [1]. The importance of chloride ions in reinforcement corrosion has led to the concept of a chloride threshold level, namely the chloride content at the depth of steel necessary to initiate corrosion-induced deterioration [2]. It is widely perceived that the chloride threshold for corrosion induced deterioration in steel reinforced concrete is best expressed as the chloride to hydroxyl concentration ratio present in the electrolyte in the concrete pores [3,4]. This implies that bound chloride presents a negligible corrosion risk and dissolved hydroxyl ions are the principal inhibitors in concrete [5,6].

Recent work has questioned this hypothesis [7–9]. Indeed an analysis of the available experimental evidence suggested that, on balance, the chloride binding capacity has little influence on the corrosion risk at a given total chloride level [8,10]. This implies that bound chloride may present a corrosion risk and contributes to the reservoir of available chloride at the steel concrete interface. For example, chloride that is bound in compounds like Friedel's salt will become available following a local fall in the pH [11] and the pH-dependent dissolution characteristics of chloride bound in an ordinary Portland cement (OPC) concrete have previously been measured [12]. This pH reduction may be induced by pit nucleation and such a change in the local environment is widely believed to be necessary to sustain pit growth and prevent repassivation [13,14]. Thus bound chloride will become available to sustain passive film breakdown [7,8].

In addition to the corrosion risk presented by bound chloride, the adequacy of the pore solution hydroxyl concentration as a measure of the inhibitive properties of the cement has been questioned [15,16]. Not only does it present little resistance to a local reduction in pH, but high levels of soluble hydroxyl ions will dissipate long before chloride ions reach the steel in sufficient quantity to initiate corrosion. The acid neutralisation capacity of precipitated hydroxides appears to be more important than the soluble hydroxyl content in resisting a local fall in pH to values below that required to sustain a passive film [17–19]. In terms of the currently used representations, it was therefore concluded that chloride threshold levels are best presented as total chloride contents expressed relative to the weight of cement. This may be viewed as the total aggressive ion content expressed relative to the total inhibitor content [20].

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Table 1
The oxide composition of OPC, SRPC, and CAC

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	Mn_2O_3	TiO_2	SO_3	Ig. loss
OPC	64.7	20.7	4.6	3.0	1.0	0.13	0.65	–	–	3.0	1.3
SRPC	62.9	21.2	3.8	5.1	0.4	0.2	0.45			2.1	1.2
CAC	39.3	4.0	38.0	16.0	0.1	–	–	–	1.7	–	0.7

This work extends previous work by characterising the pH-dependent solubility of chloride and the acid neutralisation capacity of concretes with different chloride binding capacities. The tests reported here were conducted on concretes made with three different binders, namely OPC, a blend of OPC and 10% calcium aluminate cement (CAC) and sulphate resisting Portland cement (SRPC).

2. Experimental

Concrete specimens were made using 275 kg m^{-3} cementitious binder, 680 kg m^{-3} fine aggregate (grade M sand) and 1230 kg m^{-3} 10 mm aggregate. The free *w/c* ratio was 0.4. The binders used were OPC, SRPC, and CAC. The specimens were sealed in plastic and cured in the laboratory for 30 days. The oxide compositions of these binders are given in Table 1. The specimens were exposed to a neutral 4 M chloride solution for 17 months to facilitate chloride ion contamination. Approximately 200 g of the chloride contaminated concrete was ground in a sealed container to produce powdered samples with a particle size of less than 200 μm. A batch of 18 tests was undertaken to determine the acid neutralisation capacity of each specimen. The output of each test was the steady-state pH resulting from the addition of a predetermined quantity of nitric acid to 5 g of ground concrete sample that initially had been suspended in 5 ml of deionised water (the total volume of liquid added was made up to 11 ml using deionised water). A small sample of solution was separated from each suspension using a centrifuge and analysed for chloride by potentiometric titration against silver nitrate. Further experimental details have previously been reported [12,16].

3. Results

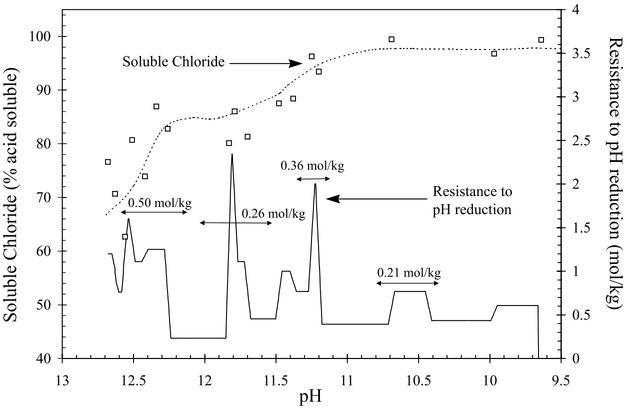

Fig. 1. The soluble chloride content and resistance to reduction in pH determined on chloride contaminated OPC concrete.

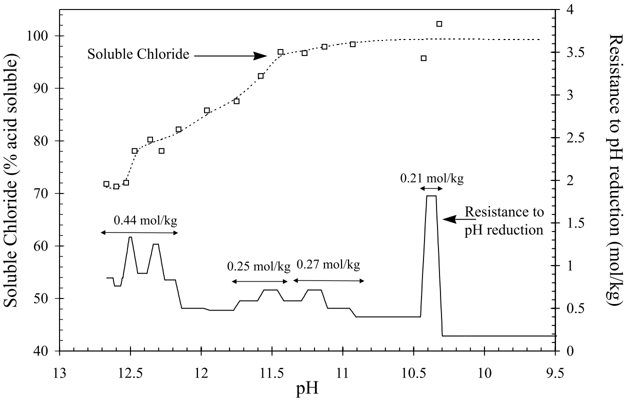

Fig. 2. The soluble chloride content and resistance to reduction in pH determined on chloride contaminated SRPC concrete.

Figs. 1–3 show the pH dependent behaviour of the soluble chloride content expressed as a percentage of the soluble chloride content at pH of 9. The steady-state pH values were determined 10 days after adding the acid. The ground sample was suspended in water prior to adding the acid to minimise the evolution of gas that sometimes occurred on adding the acid. The soluble chloride content of the suspension to which no acid was added was approximately 65% for OPC (Fig. 1), 70% SRPC (Fig. 2) and 50% for 10% CAC (Fig. 3). As the pH is decreased from an initial value of 12.75 the amount of soluble chloride increased. Most of the acid soluble chloride is released before the pH falls to 11. Sharp increases occur between pH 12.5 and 12 and between pH 11.5 and 11.

Also included in Figs. 1–3 is the resistance to pH reduction presented by the various concretes containing chloride. These curves were obtained by transforming the titration data (acid added versus final pH obtained in the test) using a process known as differential acid neutralisation analysis [21]. This process essentially

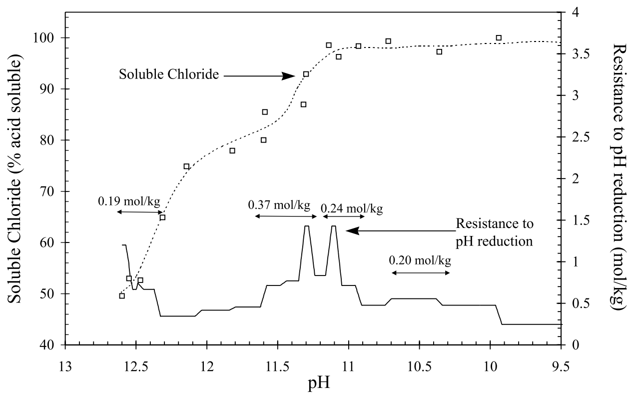

Fig. 3. The soluble chloride content and resistance to reduction in pH determined on chloride contaminated 10% CAC concrete.

Table 2
The estimated quantity of acid required to produce pHs of 12, 11 and 10

Specimen	Acid (mol/kg) to produce pH 12	pH 11	pH 10
OPC–Cl^-	0.56	1.27	1.79
SRPC–Cl^-	0.58	1.17	1.66
10% CAC–Cl^-	0.33	1.06	1.58

involves inverting the first derivative of the titration data. The results have been smoothed using a moving average process [16]. Peaks occur at pH values where greater resistance to a reduction in pH was encountered. While there were some differences between OPC, SRPC and 10% CAC, strong peaks were observed at pH values between 12.5 and 12 and 11.5 and 11 in all the samples tested.

The estimated quantity of acid required to produce pHs of 12, 11 and 10 is given in Table 2. The OPC concrete presented the greatest resistance to reduction in pH followed by SRPC and then 10% CAC.

4. Discussion

4.1. Mechanism

Steel is normally passive in concrete. The type of corrosion that occurs may be defined as pitting corrosion although the pits tend to be relatively shallow. In developing the mechanism for the participation of solids in corrosion initiation it should be noted that corrosion initiation requires both pit nucleation and pit growth. There is much debate concerning the mechanism of pit nucleation in many environments where pitting occurs [13]. However this is only the first stage of corrosion initiation. According to one prominent textbook "most pits die at the nucleation stage" [22]. It is generally accepted that a low pH of the pit solution coupled with an increase in the aggressive ion content are critical factors that prevent repassivation. A pH below 9 is necessary to render the passive film thermodynamically unstable [13] and, if it remained at higher values at the site of a nucleating pit, metal dissolution may well be accompanied by passive film formation thus stifling pit growth. Local acidification and the establishment of pH gradients may result from the reaction of metal cations with water and hydroxyl ions to form insoluble products, while the charge imbalance created will be neutralised by the ingress of aggressive anions such as chloride ions. Thus the growth of pits is essentially being catalysed by their reaction products [13,22].

When applying this to the case of reinforced concrete, it may be noted that the transient dissolution of metal from the steel during a pit nucleation event that is followed by repassivation would go unnoticed. Changes in the local environment that would allow pits to grow are essential if corrosion-induced deterioration is to be observed. The inhibitive effect of the solid phases of cement hydration arises because many of these will resist the necessary local fall in pH that might otherwise be induced by a pit nucleation event. In the process of resisting a fall in pH, most of the chloride bound in the solid phases may be released. Thus the corrosion risk presented by bound chloride at the steel–concrete interface may be similar to that presented by the free chloride as such chloride is available to support the formation of stable pits [7,12].

4.2. The pH-dependent solubility of chlorides in concrete

The results (Fig. 1) show that 10% CAC released the most bound chloride expressed as a percentage of total soluble chloride while SRPC released the least chloride. The amount of bound chloride released is dependent on the chloride binding capacity of the cement. It is evident that almost all the bound chloride is released before the pH falls to 11. These chloride ions would therefore become available during the formation of a stable pit to promote metal dissolution.

In a previous work [12], where the final pH was obtained in 3 days, two phases binding chloride that decomposed at pH values of 12.4 and 12 were identified. In this work sharp increases in the soluble chloride content at pH values of 12.4 and 11.3 were observed after 10 days. The release of chloride was again associated with peaks in the resistance to pH reduction corresponding to the dissolution of the chloride-containing phases. It is postulated that the chloride binding phase at pH 11.3 that was not previously detected could be the result of the longer duration of the test which may allow precipitation of some of the chloride initially released at higher pH values.

4.3. Resistance to pH reduction

The added acid per unit of pH reduction gives the resistance to the reduction in pH or the buffering index. In this work the acid neutralisation capacity of concrete is defined as the quantity of acid added to achieve the pH reduction to 10. Many phases present in hydrated cement are capable of resisting a fall in pH [16,23,24]. While SRPC is expected to produce a similar quantity of calcium hydroxide to OPC during hydration, SRPC has a lower acid neutralisation capacity than OPC (Table 2). Similar observations have been reported in previous work [16,23]. These differences are probably due to variations in the quantity of other important hydration products produced. 10% CAC has the lowest acid neutralisation capacity.

A local resistance to pH reduction will inhibit pit growth and promote repassivation. In the past, calcium hydroxide has been considered to be the principal solid phase that inhibits corrosion at the site of a nucleating pit. However, the presence of several peaks in the acid neutralisation behaviour measured shows that other phases of hydrated cement have similar properties to that of calcium hydroxide. All of these phases inhibit the pore solution pH in concrete from falling below 10 [16,20].

5. Conclusions

1. Most of the acid soluble chloride in concrete will enter the pore solution following a reduction of its high initial pH to a value of 11. These chloride ions will therefore be available at the site of a nucleating pit long before the local pH falls to a value necessary to sustain pit growth and prevent repassivation. This supports the previous hypothesis that chloride which is bound at the typical values of the pore solution pH (>12.5) may present a corrosion risk.

2. Significant increases in the soluble chloride content were observed as pH values were reduced below 12.4 and 11.3. These values were relatively independent of the cement type. However they do differ from the values 12.4 and 12, previously reported. This difference may arise from the longer duration of the present tests allowing the precipitation of some of the chloride initially released at a higher pH in a phase not previously detected.

3. The acid neutralisation capacity may be defined as the acid required to achieve a given pH. This depends on the cementitious binder decreasing in the order OPC $>$ SRPC $>$ 10% CAC. There are several solid phases which are responsible for the resistance to acidification.

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