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FACTORS INFLUENCING ELECTROCHEMICAL REMOVAL OF CHLORIDE FROM CONCRETE

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ABSTRACT

Electrochemical chloride removal was studied using prisms made from concrete containing various levels of chlorides derived from sodium chloride added during mixing. The amount of chloride removed during the treatment was assessed by analysing the anolyte. Chloride removal increased with increasing applied potential, number of reinforcing bars at a particular depth and initial chloride content of the concrete. A greater percentage of chloride was removed from prisms where the thickness of the chloride bearing layer of concrete was less than the depth of cover to the reinforcement. Where the thickness of the chloride bearing layer exceeded the cover to the reinforcement, the use of an external cathode significantly increased the total amount of chloride removed. Chloride removal from a face remote from the source of the chloride contamination (soffit desalination) was shown to be feasible.

Introduction

Chloride-induced corrosion of steel reinforced concrete structures remains a major problem worldwide. One means of rehabilitating structures suffering from this type of attack is the removal of offending chloride from concrete using an electromigration technique popularly referred to as desalination.

Desalination involves mounting an anode surrounded by a liquid electrolyte on the surface of the concrete and passing direct current between the embedded reinforcement, which acts as a cathode, and the anode. The current results in chloride ions being drawn towards the anode. On reaching the surface they eventually pass into the anolyte and are thereby removed from the concrete [1].

This approach is claimed to offer many advantages over existing methods of treating chloride contaminated concrete such as relatively short treatment times and no ongoing maintenance costs [2]. However, recent studies suggest that even prolonged treatment will remove only 40-55% of the total chloride [3]. Concern exists therefore regarding the length of time for which a desalination treatment stops corrosion of the reinforcement.

This paper reports on an preliminary investigation into the factors influencing the electrochemical removal of chloride from concrete. The study is based on testing concrete prisms containing internal chloride derived from sodium chloride and measuring the chloride content of the anolyte.

Test Parameters

The effect of the following parameters on electrochemical chloride removal was studied:

1. applied potential gradient
2. reinforcement arrangement
3. initial chloride content
4. depth of chloride contamination with respect to cover to the reinforcement
5. use of an external cathode
6. soffit desalination i.e. chloride removal from a face remote from the source of the contamination.

For parameters (2)-(6) a constant potential of 20V was applied. The amount of chloride removed during the treatment was assessed by analysing the anolyte. This method was selected for ease of use and the fact that it gives good correlation with the results obtained by measuring the chloride remaining in concrete [4].

Investigations on chloride binding in concrete show that chlorides introduced at the time of mixing (internal chloride) behave similarly to chlorides which penetrate once the concrete has hardened (external chloride) [5]. Therefore, although specimens containing external chloride would have been more representative of conditions found in practice, concrete specimens containing internal chloride were used in this study since it was easier to assess the efficiency of the process.

Experimental Procedure

The tests were carried on concrete prisms, 200mm × 200mm × 120mm high, containing one, two or three 10mm diameter mild steel bars arranged as shown in Fig. 1. Welded tip PTFE insulated type K thermocouples were cast into a number of the specimens containing one and three bars to measure temperature changes in the concrete during the treatment. A perspex frame, cast into the top face of each prism, served to contain the electrolyte/electrode system.

The composition of the concrete is shown in Table 1. In one set of prisms the concrete was dosed throughout with either 2%, 3% or 4% Cl (by weight of cement) from NaCl. In the other set the prisms were cast using two layers of concrete; a chloride free bottom layer and a chloride rich top layer. The chloride contents and the thicknesses of the chloride rich layers of concrete are shown in Table 2.

The prisms were cast in timber moulds and cured for one day beneath polythene sheeting. Thereafter, they were demoulded and stored in a room at 95 ± 2% relative humidity and 21 ±

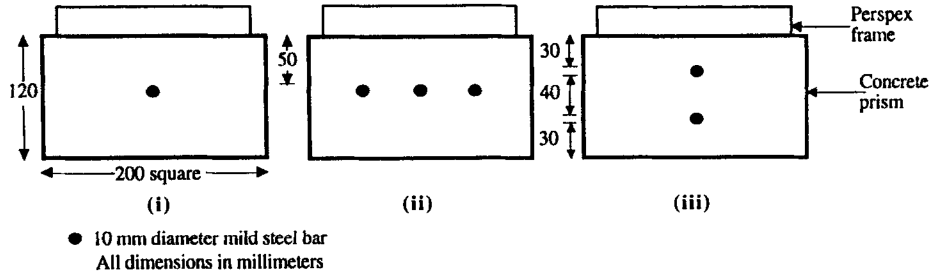


FIG. 1.
Test specimens.

1 °C. At the appropriate age, the prisms were desalinated using one of the arrangements shown in Fig. 2. Generally, desalination was carried out by passing a direct current between the embedded reinforcing steel and an anode system, attached to the top of the prism, consisting of an inert catalysed titanium mesh immersed in 0.1M NaOH solution (Fig. 2a). In some specimens the anode was connected to an external cathode consisting of titanium mesh immersed in water, attached to the bottom surface of the prism, in addition to the embedded reinforcement (Fig. 2b).

Desalination was also carried out by attaching the anode to the bottom face of some prisms (soffit desalination) and passing direct current between either (i) the reinforcement and the anode (Fig. 2c) or (ii) the reinforcement plus an external cathode, attached to the top face of the prism, and the anode (Fig. 2d). Table 2 gives details of the particular operating conditions applicable to each prism.

The NaOH solution was replaced every 2 to 3 days to maintain alkalinity and prevent chlorine gas from being evolved from the electrolyte. Desalination was normally continued until the rate of chloride extraction was negligible.

The chloride removed during the treatment was determined periodically by potentiometrically titrating 2ml aliquots of the electrolyte with a silver nitrate solution using a chloride ion selective electrode, in accordance with the method described by Berman [6]. Two replicates of each prism were tested.

Results and Discussion

Applied Potential. Fig 3 shows a plot of the amount of chloride removed as a function of the fixed applied potential for prisms containing one bar (Fig. 1(i)) and desalinated from the top surface (Fig. 2a). It can be seen that the rate and total amount of chloride removed increases with increasing applied potential. This effect is almost certainly attributable to an increase in current flow with increasing applied potential (Fig. 4).

TABLE 1
Mix Details (Proportions by Weight)

OPC	1.00
Sand (zone 3)	2.40
10mm aggregate (limestone)	2.90
water	0.65

TABLE 2
Test Details

Specimen type †	Depth of chloride rich layer (mm)	% Cl *	Age (days)	Test set-up†	Applied potential (V)
(i)	75	1.87	80	(a)	10
(i)	75	1.87	80	(a)	20
(i)	75	1.87	80	(a)	30
(i)	75	1.87	80	(a)	20
(ii)	75	1.87	80	(a)	20
(i)	120¥	2	28	(a)	20
(i)	120¥	3	28	(a)	20
(i)	120¥	4	28	(a)	20
(i)	25	3	28	(a)	20
(i)	50	3	28	(a)	20
(i)	120¥	3	28	(a)	20
(iii)	120¥	3	28	(a)	30
(iii)	120¥	3	28	(b)	20
(i)	50	3	28	(a)	20
(i)	50	3	28	(c)	20
(i)	50	3	28	(d)	20

† see figure 1. † see figure 2. * chloride by weight of cement from NaCl ¥ full depth

Fig. 4 also shows that the current in the prisms generally decreases with treatment time which suggests that the concrete resistance increases. This may be related to the reduction in the chloride content of the prisms. There is also some evidence that this effect results from a redistribution of the $Ca(OH)_2$ from the cement paste matrix by a dissolution and reprecipitation process [7].

Number of Bars. Fig. 5 shows the effect on chloride removal from prisms containing one (Fig. 1(i)) and three reinforcing bars (Fig. 1(ii)) and desalinated from the top face (Fig. 2a) using a constant potential of 20V (Table 2). It can be seen that for a given treatment time, greater amounts of chloride are removed from specimens containing three bars rather than one bar. This difference is probably due to the higher currents (Fig. 6) and the fact that there is a larger cathodic area, and hence a larger electric field, in the prisms containing three bars.

Fig. 6 also shows that the charge passed in the prism containing three bars is approximately 4.6 times greater than in the prism containing one bar. However the total amount of chloride removed from the prism with three bar is only around 1.4 times higher (Fig. 5). This suggests that much of the extra charge does not contribute to chloride removal. Thermocouple reading show that the temperatures in the prism containing three bars increased by around 15°C above the ambient during the treatment, whereas in the prism containing one bar the temperature increased by about 1°C.

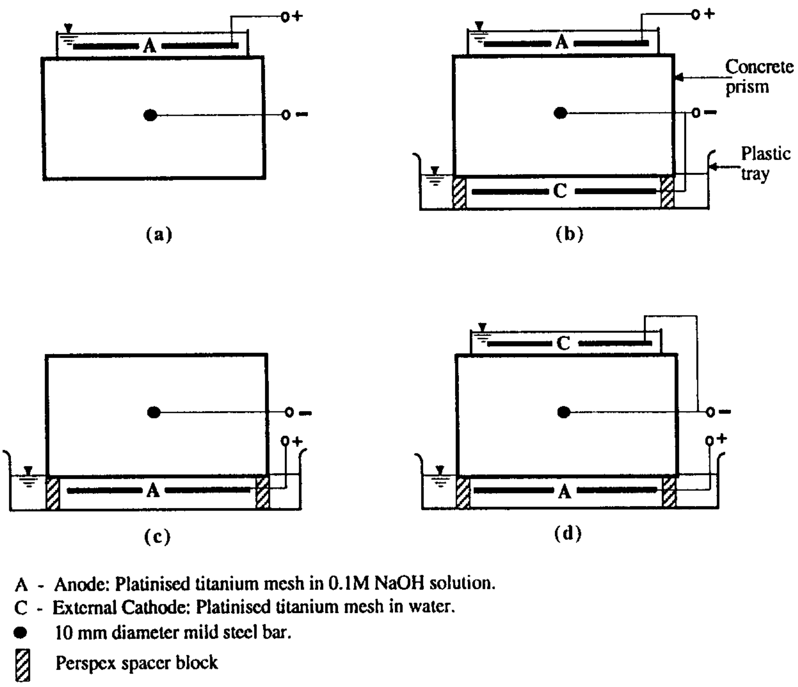
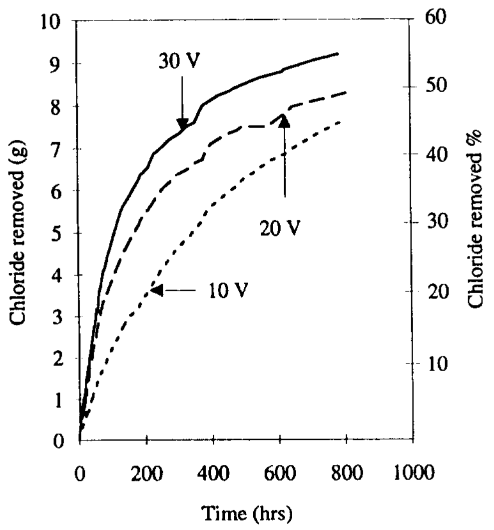


FIG. 2.
Desalination set-ups.



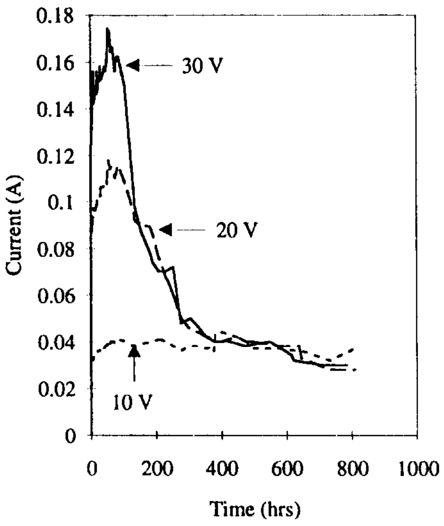


FIG. 3.
Effect of potential difference on chloride removed.

FIG. 4.
Influence of potential on current.

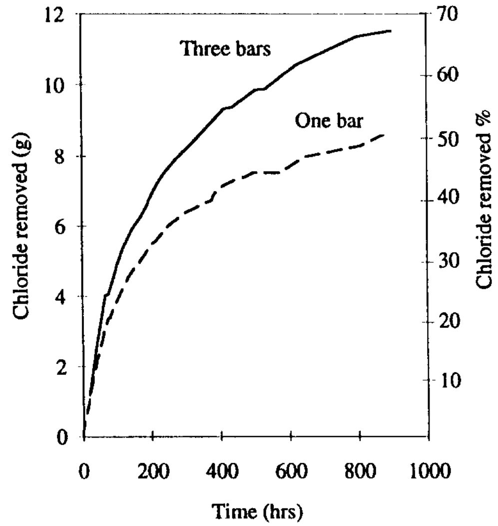


FIG. 5.
Chloride removed from prisms containing one or three bars.

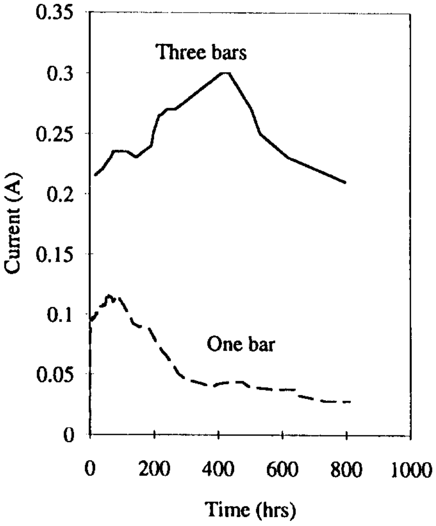


FIG. 6.
Influence of number of bars on current.

Initial Chloride Content. Fig. 7 shows the amount of chloride removed from prisms containing one steel bar (Fig. 1(i)) and made from concrete dosed with either 2%, 3% or 4% Cl (by weight of cement). All the prisms were desalinated from the top face using the set-up shown in Fig. 2a. It can be seen that the amount of chloride removed increases with increasing initial chloride

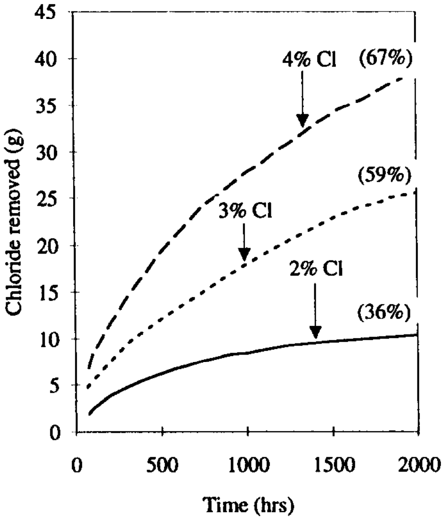


FIG. 7.
Effect of initial chloride content on chloride removed ( ) max % removed at 2000 hrs.

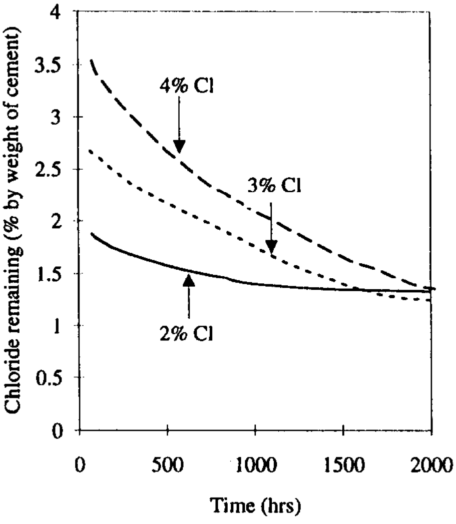


FIG. 8.
Effect of initial chloride content on chloride remaining.

content. This is probably due to the fact that, for a given cement type, the percentage of free chloride increases with increasing total chloride content [8] and the resistance decreases with increasing chloride content.

If the data are re-plotted as in Fig. 8, it can be seen that the average amount of chloride remaining in the specimens is approximately 1.3% Cl (by weight of cement), irrespective of the initial dosage level. This implies that it is the free rather than the bound chloride that are removed during desalination. While this may be generally true, there is some evidence that in the vicinity of the reinforcement both the free and a proportion of the bound chloride are removed [9,10].

Depth of Chloride Contamination. Fig. 9 shows the amount of chloride removed from three pairs of prisms containing one bar with a concrete cover of 50mm (Fig. 1(i)) and made with either the top 25mm, 50mm or 120mm (i.e. full depth) layers of concrete dosed with 3% Cl (by weight of cement). The prisms were all desalinated from the top face (Fig. 2a). Chloride removal appears to be most efficient in the case of prisms containing chlorides in the top 25mm layer of concrete (Fig. 10). This is presumably due to the fact that this gives the greatest overlap of the electric field between the anode and cathode with the chloride-rich layer of concrete in the prism.

Fig. 9 also shows that the amount of chloride removed from prisms made with the top 50mm layer of concrete dosed with chlorides was less than the prisms made wholly from chloride bearing concrete. Since the cover to the reinforcing bar is also 50mm, the results suggest that a proportion of the chloride behind the reinforcement is removed during desalination. One way of further increasing the amount of chloride removal from behind the reinforcing bars may be to use an external cathode as discussed next.

External Cathode. Tests to determine chloride removal efficiency using an external cathode were carried out on prisms containing two bars with a vertical separation of 40mm (Fig. 1(ii)).

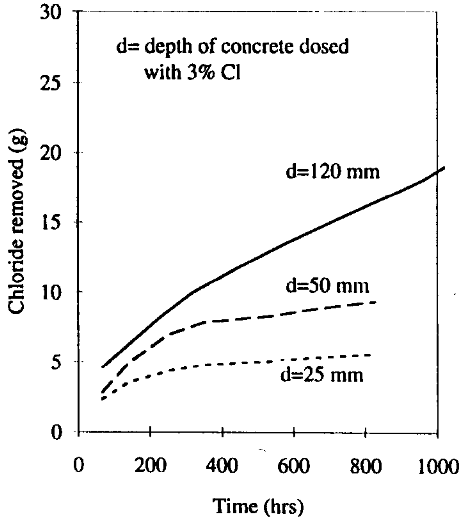


FIG. 9.
Effect of depth of chloride content on chloride removal.

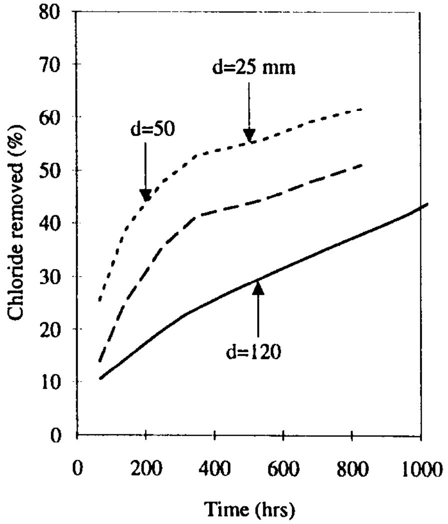


FIG. 10.
Effect of depth of chloride content on chloride removal efficiency.

The anode was attached to the top face of the prism and direct current passed either between the embedded bars and the anode (Fig. 2a) or between both the embedded bars and an external cathode, which was attached to the bottom face of the prism, and the anode (Fig. 2b). From the results in Fig 11 it can be seen that the amount of chloride removed is greater when an external cathode is used. Presumably this is due to the fact that the external cathode enables chloride to be removed more easily from the region between the reinforcement and the external cathode.

Soffit Desalination. Desalinating a bridge deck from the soffit would be desirable since the treatment could then be applied without the need to interrupt traffic flow. Therefore, a brief study was carried out to compare chloride removal from prisms using conventional and soffit desalination. The prisms all contained one bar (Fig. 1(i)) and the top 50mm layer of concrete was dosed with 3% Cl (by weight of cement) to simulate chloride contamination of the top surface of the deck.

From the results in Fig. 12 it can be seen that the amount of chloride removed is far greater if desalination is carried out from the top surface (Fig. 2a) rather than the soffit of the prism (Fig. 2c). However, the amount of chloride removed from the soffit can be significantly increased using an external cathode (Fig. 2d) although this would interfere with traffic movement.

Half cell potential readings showed that corrosion had ceased at the end of 1000 hours in all cases. This was in spite of the fact that a larger percentage of chloride remained in the prisms subject to soffit desalination. On this basis it would seem that, perhaps, the main positive aspect of this treatment is that chlorides are repelled away from the bar and not necessarily that chlorides are totally removed from the concrete. The variation of chloride concentrations with distance from the reinforcing bar at the end of the treatment may determine the long term effectiveness of desalination.

Overall Remarks on Chloride Removal. At the outset it was pointed out that previous studies have shown that between 40-55% of the total chloride can be removed after desalination. From the results presented here it can be seen that if the depth of chloride contamination is less than

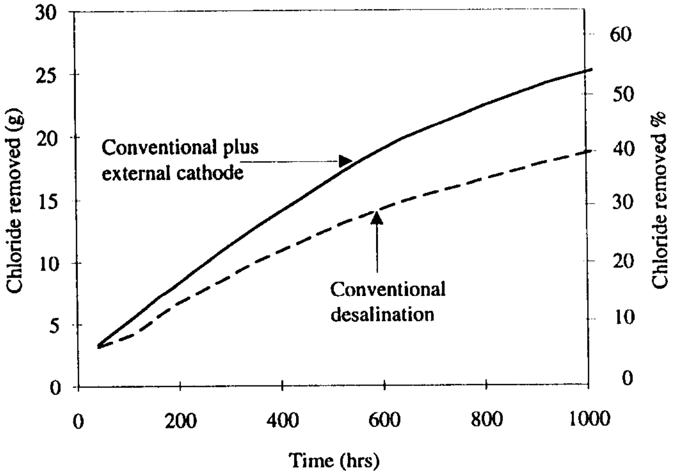


FIG. 11.
Effect of an external cathode on chloride removal.

or equal to the cover to the reinforcement, between 55%-65% of the total chloride can be removed after prolonged periods of desalination (Fig. 9). Where the depth of chloride contamination exceeds the cover to the reinforcement, the maximum amount of chloride removed appears to be around 40% (Fig. 9) but can be increased if an external cathode is used (Fig. 11).

Increasing the applied potential (Fig. 4) and/or the number of reinforcing bars at a particular depth (Fig. 6) significantly increases the current. However, doubling the current does not double the amount of chloride removed (Figs 3 & 5) and can lead to a significant increase in the temperature of the concrete.

The amount of chloride removed from specimens with either 2%, 3% or 4% Cl was, respectively, 36%, 59% and 67% (Fig. 7) at 2000 hours. However, the chloride remaining in the specimen was around 1.3% Cl (by weight of cement) irrespective of the initial chloride content (Fig. 8) which implies that only the free chloride may be removed during desalination.

Conclusions

1. The amount of chloride removed increases with increasing applied potential and number of reinforcing bars at a particular depth.
2. Higher initial chloride contents result in greater amounts of chloride removal but the chloride remaining was found to be independent of the initial chloride content.
3. Greater proportions of chloride are removed from specimens where the depth of chloride contamination is less than the depth of the reinforcing bars.
4. Where chlorides exist at levels deeper than or adjacent to the reinforcing steel, an external cathode positioned at the face remote from the source of chloride can be used to increase chloride removal.
5. Electrochemical removal of chlorides from a face remote from the source of chloride

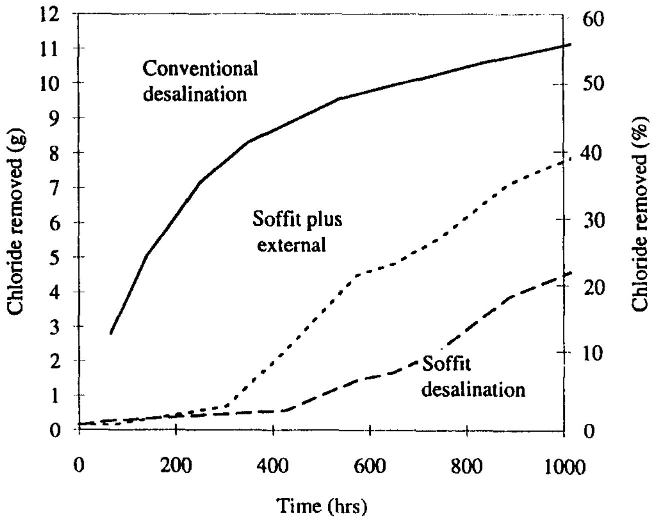


FIG. 12.
Effect of soffit desalination on chloride removal.

contamination (soffit desalination) has been shown to be a feasible option for arresting corrosion.

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