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CHLORIDE THRESHOLDS IN MARINE CONCRETE

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ABSTRACT

This paper reports results from an ongoing study of the performance of fly ash concrete in marine exposure. Reinforced concrete specimens exposed to tidal conditions were retrieved at ages ranging from 1 to 4 years. Steel reinforcement mass losses are compared with chloride contents at the location of the bar for concrete specimens of various strength grades and with a range of fly ash levels. The maximum level of chloride that could be tolerated without significant mass loss due to corrosion was found to vary with fly ash content. This threshold chloride level decreased with increasing fly ash content; values obtained were 0.70%, 0.65%, 0.50% and 0.20% acid-soluble chloride (by mass of cementitious material) for concrete with 0%, 15%, 30% and 50% ash, respectively. Despite the lower threshold values, fly ash concrete was found to provide better protection to the steel under these conditions, due to its increased resistance to chloride ion penetration.

Introduction

It has long been recognized that chloride ions can induce a state of active corrosion of steel in reinforced concrete (1). However, the relationship between corrosion and the concentration of chlorides at the steel is complex. Early studies (2,3) showed that the risk of corrosion of steel in chloride solutions increases with the $[Cl^-/OH^-]$ ratio of the solution, and a critical ratio of 0.61 was proposed (2). However, no particular threshold value for steel corrosion in concrete has been universally accepted.

It has become common practice to limit the permissible chloride content of reinforced concrete as a percentage of the cement, values of 0.40% (acid-soluble) or 0.15% (water-soluble) by mass of cementitious material being commonly used in Europe and North America, respectively. However, for a given chloride/cement ratio in concrete, the $[Cl^-/OH^-]$ ratio of the pore solution at the steel is affected by a wide range of parameters (particularly cement composition) and is difficult to predict or even to determine by chemical analysis. Consequently, the threshold chloride content is likely to vary widely between different concretes, as shown by the wide range in reported values (4), and the adoption of a single value for the purpose of specification or service life prediction is inappropriate.

The incorporation of supplementary cementing materials into concrete is known to have a profound effect on the pore solution composition and, therefore, may be expected to alter the

TABLE 1

Chemical Analysis

	OPC	Ash 1	Ash 2	Ash 3
SiO_2	20.55	48.2	48.1	52.4
Al_2O_3	5.07	26.7	24.0	26.0
Fe_2O_3	3.10	11.6	10.6	9.4
CaO	64.51	1.71	6.12	1.69
MgO	1.53	1.62	1.61	1.54
K_2O	0.73	3.18	1.83	2.87
Na_2O	0.15	0.65	0.79	1.32
SO_3	2.53	0.83	0.90	0.85
LOI	1.58	4.34	4.49	2.80
<45μm		11.3	19.5	5.53
C_3S	57			
C_2S	16			
C_3A	8			
C_4AF	9			

TABLE 2

Concrete Mix Proportions

	Ash cont. (%)	Cement (C+F) (kg/m^3)	W/(C+F)	Slump (mm)	28-d cube strength (MPa)
C25	0	250	0.68	60	32.5
	15	266	0.61	55	33.0
	30	289	0.54	30	34.5
	50	324	0.44	40	33.0
C35	0	300	0.57	50	41.5
	15	319	0.51	45	44.5
	30	346	0.45	40	45.5
	50	392	0.37	30	41.5
C45	0	350	0.49	40	50.0
	15	369	0.44	35	50.0
	30	400	0.39	50	53.0
	50	452	0.32	30	48.0

threshold chloride content for corrosion. The use of fly ash, for instance, has been shown to increase the chloride binding capacity of hydrates thus reducing the level of chlorides in the pore solution (5,6). However, ash is also efficient in reducing the pore solution alkalinity and may actually increase the $[Cl^-/OH^-]$ ratio of the pore solution compared with control samples at the same total chloride content (7). Such behaviour may be expected to lower the threshold chloride content in fly ash concrete and, although this has not been adequately demonstrated, studies have shown higher corrosion rates in fly ash concrete at specific chloride contents despite increased binding of the chlorides (8).

This paper reports some of the results from an ongoing study of the marine performance of fly ash concrete. Reinforced concrete specimens of various strength grades and with a range of fly ash replacement levels, have been exposed to marine tidal conditions for periods of up to 4 years. Relationships between reinforcement mass loss and the chloride concentration at the level of the steel are presented for the different concrete mixes to provide an assessment of the effect of fly ash on the threshold chloride concentration for the initiation of corrosion.

Experimental Studies

A single Portland cement and three sources of fly ash (equivalent to ASTM Type F) were used in this study and results of chemical analysis are given in Table 1. Three series of concrete mixes with design strengths of 25, 35 and 45 MPa, and with slumps in the range 30–60 mm were designed with a range of fly ash levels; details of mix proportions are given in Table 2. The basis for comparison within a single mix series is equal 28-day strength and workability for concrete with and without fly ash. This results in increasing cementitious contents and decreasing water contents with fly ash level.

Specimens cast from each mix included 100 mm × 100 mm × 300 mm reinforced concrete prisms with four pre-weighed 10 mm diameter mild steel bars at cover depths of 10 mm or 20 mm. These prisms were demoulded at 24 hours and exposed to a wide range of curing environments (temperature ranging from 5°C to 20°C and relative humidity from 40% to 100%) for

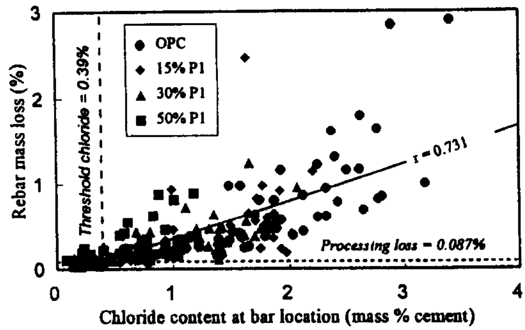


FIG. 1.
Rebar mass loss vs. Cl content for all mixes.

a subsequent period of 27 days. At 28 days, prisms were placed in the tidal zone of the BRE marine exposure on the Thames Estuary in Essex, U.K.

After exposure periods of 1, 2 and 4 years specimens were retrieved for chloride analysis and reinforcing steel mass loss. Powder samples were drilled from each prism in 5 mm depth increments (disregarding the surface 1 mm) and analyzed for acid soluble chlorides. Then the steel bars were removed, cleaned (in dilute HCl) and weighed, and the mass loss due to corrosion determined. Full details of the analytical techniques, the range of curing conditions and the marine exposure conditions have been reported elsewhere (9,10).

Results

Between 1988 and 1994, 136 reinforced concrete prisms were retrieved from the exposure site after exposure periods of between 1 and 4 years. Each prism had two steel bars at each cover depth, and the average mass loss of each pair of bars is plotted against the chloride content at the location of the steel in Figure 1. The actual values shown are the chloride contents corresponding to depth increments 11–16 mm and 21–26 mm plotted against the mass loss of the bars with 10 mm and 20 mm cover, respectively. Also shown in Figure 1 is the "processing mass loss" which was determined for 16 bars removed from four prisms which had been stored under laboratory conditions for 1 to 4 years. Although these bars were not subject to active corrosion, they were put through the same acidic cleaning process used to remove rust deposits from corroded bars. The mean mass loss of the uncorroded bars was 0.087% with a standard deviation of 0.0115%. Generally, the steel mass loss increases with chloride concentration and regression analysis of the data produces the following relationship between the mass loss (m) and the chloride content (Cl):

$$m = -0.086 + 0.442\, Cl^{-} \qquad \text{Eqn. 1}$$

For the mass loss to exceed the processing loss of 0.087%, the above relationship yields a threshold chloride concentration of 0.39% by mass of cementitious material. This value is close to the 0.40% maximum value frequently used for specification purposes. However, closer inspection of the data shows that there is no single relationship between the chloride content and

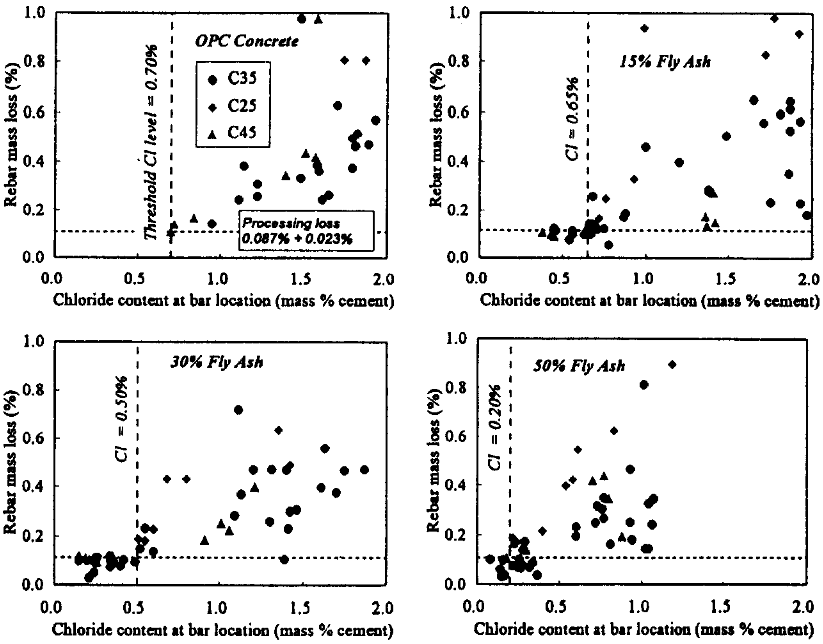


FIG. 2.
Effect of fly ash on chloride threshold content.

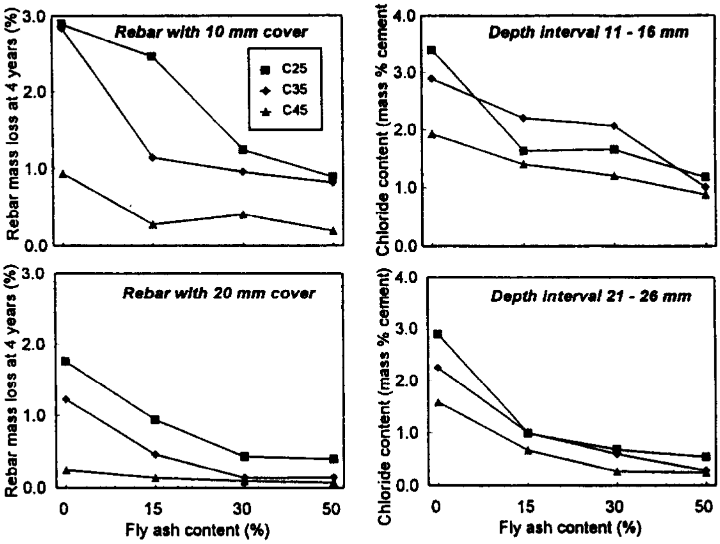
mass loss for different concrete, concrete with high levels of fly ash showing markedly higher mass loss for a given chloride level compared with the control.

Figure 2 shows the data plotted separately for mixes with different levels of fly ash. The processing mass loss is shown as the mean value (twice the standard deviation (i.e. 0.087% ± 0.023%). Any mass loss in excess of this range may be considered to indicate a statistically significant level of corrosion of the steel. From these relationships it is possible to determine the maximum level of chloride observed without significant corrosion (mass loss) for each concrete. These "threshold" values vary according to the level of fly ash as follows:

Fly ash level (%)	Threshold Cl (%)
0	0.70
15	0.65
30	0.50
50	0.20

It should be noted that chloride contents in excess of these values do not necessarily result in a significant mass loss in every case. The actual mass loss (i.e. amount of corrosion) depends on other factors such as the resistivity and oxygen availability within the concrete, which may vary between samples of the same ash content depending on the water/cementitious material ratio and the initial curing regime used.

The presence of fly ash appears to decrease the level of chlorides required to initiate corrosion, the effect being particularly dramatic at high levels of ash. Despite the lower threshold



(a) Rebar mass loss (b) Chloride concentration

FIG. 3.
Effect of fly ash on concrete performance after 4 years exposure.

values, lower steel mass losses were observed with higher fly ash levels, as illustrated by the data in Figure 3a for 4 year old concrete specimens. This is clearly attributed to the increased resistance of the fly ash concrete to chloride ion penetration as shown in Figure 3b. Indeed, for a given depth, the chloride content of C25 grade concrete with 50% ash tends to be lower than that of higher strength C45 concrete without ash.

Discussion

The data from these marine studies clearly indicate that lower chloride contents are required to initiate corrosion in concrete containing fly ash, especially at high ash replacement levels. This phenomenon was not observed in an earlier paper by the author (9), which reported one and two year data only, as few of the specimens with 50% fly ash had exhibited significant corrosion at that time. The lower threshold values are probably a corollary of higher $[Cl^-/OH^-]$ ratio in the pore solution of fly ash concrete compared with OPC concrete of the same total chloride content.

Such a result is not entirely unexpected when data from published pore solution studies is considered. Class F fly ash is known to produce a reduction in the hydroxyl ion concentration of cement paste pore solution at least in proportion to the level of ash used (11), and often to a greater extent, especially after extended periods of time (12). Thus, for concrete containing 30% ash, the OH^- concentration of the pore solution might be less than 70% of that of an equivalent concrete without ash. Fly ash is unlikely to have the same impact on the Cl^- concentration of the pore solution. For instance, the results of Arya et al. (5) show that, for chlorides penetrating into hardened concrete, the Cl^- concentration of the pore solution in a paste containing 30% fly ash might be as much as 85% of that of an OPC paste at the same total chloride content. Kawamura et al. (7) compared the $[Cl^-/OH^-]$ ratio of pore solutions in mortars with and without 30% fly ash at various levels of chloride; their results for NaCl additions were as follows:

Cl content (wt. % cement)	$[Cl^-/OH^-]$ in pore solution	
	OPC	30% fly ash
0.5	0.44	0.61
1.0	1.34	2.03
2.0	4.02	5.36

If the critical $[Cl^-/OH^-]$ ratio is taken as 0.61, as proposed by Haussman (2), these results would imply a threshold chloride concentration of 0.5% (by mass of cement) for concrete with 30% ash and a somewhat higher value for OPC concrete. Such values are consistent with the threshold values determined in the current study. Of course, the effect of fly ash on pore solution composition is dependent on a great many factors and can not be generalized; this discussion is intended merely to demonstrate the source of the lower threshold values observed for fly ash concrete.

At high levels of ash (e.g. 50% replacement by mass) there is a substantial reduction in the chloride threshold value. As the proportion of ash increases, the OH^- concentration of the pore solution would continue to increase, mainly because of the further dilution of cement alkalis. However, unpublished data by the author suggests that the smaller volume of hydrates formed at high fly ash replacement levels leads to a concomitant reduction in chloride binding. Indeed, hardened cement paste with 56% ash may actually have a higher concentration of Cl^- in solution than control pastes of the same total chloride content (the chlorides being derived from external sources).

For a given strength grade, fly ash concrete can still be expected to provide better protection to steel reinforcement, due to its increased resistance to the penetration of chloride ions. However, the lower chloride threshold values observed in this study will partially offset the benefit of using ash in chloride environments and should be considered when making service life predictions from consideration of chloride transport rates. Furthermore, the threshold value of 0.2% chloride (by mass of cementitious material) determined for concrete with 50% fly ash is considerably lower than the 0.4% acid-soluble limit used in many specifications in Europe. It is also possible that this threshold value, which refers to acid-soluble chloride, equates to a lower water-soluble than the 0.15% limit that prevails in North America. Consequently, it may be prudent to specify lower chloride limits when using high fly ash contents for reinforced concrete.

Conclusions

1. The threshold chloride contents required to initiate corrosion in reinforced concrete exposed to marine tidal conditions was found to vary significantly with the fly ash content of the concrete.
2. Increasing the fly ash content decreased the threshold chloride level; values obtained were 0.70%, 0.65%, 0.50% and 0.20% acid-soluble chloride (by mass of cement) for concrete with 0%, 15%, 30% and 50% ash, respectively.

3. Despite the lower chloride threshold levels, increasing levels of fly ash generally provided better protection to the steel reinforcement in this environment, and this is attributed to the increased resistance in chloride ion penetration.

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