

論文

[2116] A Study on Chloride Penetration in Concrete

Sudhir MISRA¹⁾ and Taketo UOMOTO²⁾

1. INTRODUCTION

Even though the exact role played by the chloride ions in the initiation and propagation of reinforcement corrosion is not fully understood, it is generally accepted that they are one of the critical factors in, at least, damaging the passivating film protecting the reinforcing bars. It can also be assumed that this passivating film is disrupted only when the chloride concentration in the neighbourhood of the reinforcing bars exceeds a certain "threshold" level. The question as to what type of chlorides are really detrimental from the view-point of reinforcement corrosion, has not been resolved. Basically, the chloride content of concrete is said to be made up of the following two parts:

1. Bound: These are chemically "trapped" in the hydration products of the cements. Generally, the tri-calcium aluminate content of cement is regarded as a measure of its chloride binding capacity⁽¹⁾. The ability of other hydration products e.g. those of silicates to bind the chlorides is not presently taken into account. And since the hydration of the aluminates is completed very rapidly, the ability of the hardened concrete to "bind" the chlorides that penetrate can be considered to be nominal.

2. Free: These are not chemically "bound" in the sense explained above, and are free to move through the pore water within the concrete on account of concentration gradients, etc., and thus travel towards the reinforcing bars through the covering concrete. However, the state in which such chlorides actually exist within the matrix is not known.

2. OBJECT OF PRESENT STUDY

This study has been carried out with the two fold objective of relating the importance of water movement in hardened concrete to the penetration of chloride ions, and to determine whether all chlorides that penetrate into "fully hydrated" concrete remain in pore solution. All specimens were cured in water for 4 months so as to "complete" the hydration process and thereby eliminate the possibility of existence of chemically bound chlorides (with C_3A) in the matrix and then immersed in salt solution.

1) Graduate student, Dept. of CE, University of Tokyo, Tokyo

2) Associate Professor, Dept. of CE, IISc, University of Tokyo, Tokyo

3. EXPERIMENTAL PROGRAMME

The sequence of operations followed in this series of experiments is shown in figure 1. 10cm x 10cm x 40cm prism specimens were cast using concrete, the proportions of which are given in Table 1. All specimens were cured in water at 20°C for 4 months. Then half of the specimens were dried out, by first leaving them in air (at 20°C) for 5 days and subsequently in an oven (80°C) for about 20 days. All specimens were then epoxy coated leaving only one face (10cm x 40cm) uncovered for allowing the penetration of water or chloride ions. A description of each of the specimens is given in Table 2. The "wet" specimens again stored in water for 2 months before immersing in solutions of 3.3% or 15% NaCl (by weight). After 1, 3 and 7 months of immersion in salt solutions, concrete powder was drilled out (using a 30mm dia drill) from various depths and analysed for total chloride content, to determine the chloride penetration profiles. The same specimen was used to determine the chloride profiles each time after the holes from the previous drilling was filled with cement paste, before reimmersing the specimen in salt solutions.

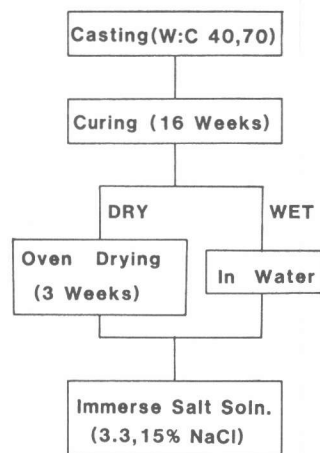


Fig. 1 Exptl. program

Table 1 Mix Proportions

W:C	W	C	S	A
40	214	534	852	903
70	220	314	937	885

Note: W, C, S, A in Kg/m³

Table 2 Specimen details

Specimen	W7-1	W7-2	W4-1	W4-2	D7-1	D7-2	D4-1	D4-2
Condition ¹⁾	Wet	Wet	Wet	Wet	Dry	Dry	Dry	Dry
W:C (%)	70	70	40	40	70	70	40	40
NaCl (%)	3.3	15	3.3	15	3.3	15	3.3	15

Note: 1) At the time of immersing in NaCl solution

4. RESULTS AND DISCUSSION

4.1 Water absorption and drying

After demolding, the specimens were weighed from time to time, and the change in weight was taken as a measure of the water absorbed or expelled. Though the results have been reported in greater detail elsewhere⁽²⁾, a brief summary for 4 of the specimens used (D4-1, D4-2, D7-1 and D7-2) is given in Table 3. These results have been obtained using the weight of the respective specimens at different times as given in the explanatory notes and Fig. 1. Comparable values (items 1 to 3, in Table 3) were obtained for W4-1, W4-2, W7-1 and W7-2, though obviously items 4 and 5 are not

Table 3 Summary of water absorption and removal from specimens

Item	Specimen no.	D4-1	D4-2	D7-1	D7-2
1)	Wt. of specimen (g)	9686	9727	9429	9369
2)	Water at casting (g)	828	832	880	875
3)	" absorbed (curing, g)	122	119	85	79
4)	" expelled (drying, g)	444	441	683	678
5)	" absorbed (salt, g)	334	357	551	589
6)	NaCl absorbed (g)	11.0	53.6	18.2	88.4
7)	" " (%)	0.12	0.57	0.21	1.01

Explanatory Notes:

- 1) Weight of specimen at demolding
- 2) Calculated on basis of unit water content (table 1) & 1 above
- 3) to 5) Change in wt. during water curing (115 days), drying (26 days) & after immersing in salt solution (28 days)
- 6) From 5 above and concentration of 3.3% or 15%
- 7) By wt. of dried concrete (6/(1+3-4))

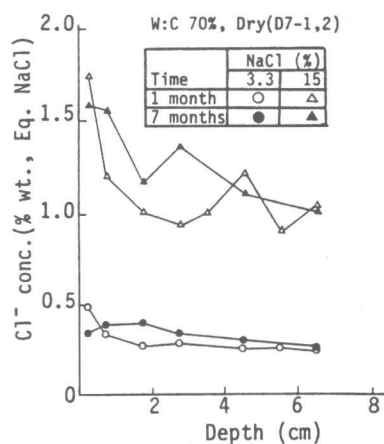
applicable in the case of the wet specimens. Changes in weight on account of penetration in this case due to diffusion were found to be negligible. By comparing the values in item 3 for D4-1, 2 with those for D7-1, 2, it is clear that concrete with a lower w:c takes in more water during curing than one with a higher w:c. In actual practice, this finding has the important implication that a concrete with a lower w:c ratio could be counter-productive unless adequately cured. Also it can be verified from table 2 that the amount of water that remains in the specimens after drying out (items 2+3-4) is in proportion to the cement content, regardless of the water cement ratio, a finding that is line with the fact that cement requires between 20 and 25% (by wt.) of water for hydration.

4.2 Cl^- penetration in hardened concrete

In this series of experiments, chloride penetration in hardened concrete occurs as two distinct processes: permeation with salt water (in combination with some sort of concentration gradient induced diffusion, as we shall see later) in the "dry" specimens, and diffusion in the "wet" specimens.

Figures 2 and 3 show the chloride penetration profiles obtained in the initially "dry" (D) specimens after 1 and 7 months of immersion in 3.3% and 15% NaCl solutions. (For the sake of clarity the results obtained at 3 months immersion have not been depicted here.)

Figure 2 for specimens D7-1, 2 suggests that because of the high water cement

Fig. 2 Cl^- penetration in concrete

ratio, the specimen is easily and rapidly saturated with the salt solution and thus the chloride profiles are more or less flat. The average value of the NaCl concentration from these profiles at one month is 0.30% and 1.14% for 3.3% and 15% NaCl solution respectively. These values are higher than 0.21 and 1.01% calculated only from the salt water absorbed (item 7, table 3). The increase in the average values at 7 month immersion to 0.34% and 1.30%, shows still continuing chloride ingress from outside. This shows that some other mechanism for chloride penetration supplements the chloride penetration with water. The weighing of the specimens was discontinued after 1 month immersion in salt water.

A study of figure 3 shows that the dense pore structure (D4-1, 2) makes the water penetration difficult. This can be determined from the fact that the chloride values rapidly reduce with depth. In this case the average chloride content from table 3 (item 7) cannot be directly compared with the obtained profiles. However, the area under the "C(x) vs. x" plots (fig 3) is a measure of the total chlorides absorbed and a comparison again shows that as in the case of D7-1 and D7-2 above, in the case of D4-1 also, the amount of Cl^- absorbed (from table 3) are much less than those determined from fig 3. Specimen D4-2, however, gives slightly anomalous results.

The profiles in figures 4 and 5 are for specimens that were saturated with water when immersed in salt water. In this case, thus, chloride penetration occurs almost purely by diffusion on account of concentration gradients and more or less expected trends caused by differences in water-cement ratio and the concentration gradients are reflected. The chloride penetration is deeper for a higher w:c ratio and increase with time. The increment too, is greater if the concrete has a higher w:c. Under these conditions, the chloride concentration $C(x,t)$ at distance "x" from surface

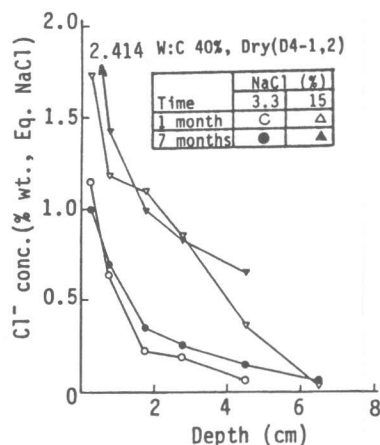


Fig. 3 Cl^- penetration in concrete

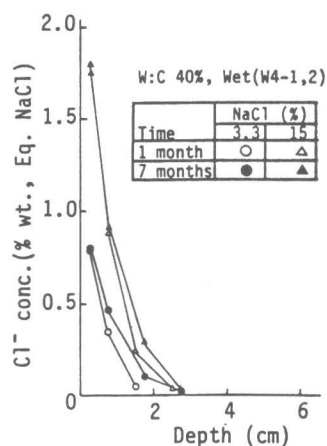


Fig. 4 Cl^- penetration in concrete

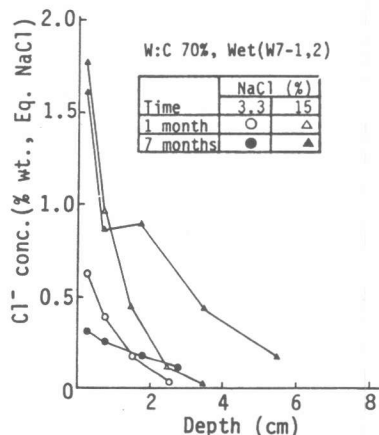


Fig. 5 Cl^- penetration in concrete

after time "t" can be obtained using Fick's law, i.e.,

$$C(x,t) = C_0(1-\text{erf}(x/\sqrt{4Dt})) \dots (1), \text{ where,}$$

C_0 is $C(0,t)$, D is the diffusion coefficient and "erf" is the error function. Using the method suggested by Nagano and Naito⁽³⁾, the values of the pseudosurface concentration, C_0 , and effective diffusion coefficient have been calculated from the profiles in figures 4 and 5, and the results are tabulated in table 4.

Table 4 C_0 and Eff. D from profiles in figures 4 and 5

Specimen	C_0 (%)		$D(10^{-8} \text{ cm}^2/\text{s})$	
	1 month	7 months	1 month	7 months
W4-1	1.2	0.9	9.3	3.7
W4-2	2.8	2.2	8.3	3.7
W7-1	0.8	0.4	29.3	20.7
W7-2	1.8	1.8	35.7	27.0

Profiles obtained using the equation (1) and the C_0 and D from table 4 are in good agreement with those obtained experimentally. But more than trying to establish the validity of the diffusion model, the object of this paper is to discuss how chloride contents as high as those shown in these figures are held in the concrete. The following paragraphs discuss a plausible model to explain the occurrence of the high concentrations of chlorides not only near the surface but also within the concrete, by hypothesising some sort of surface adsorption of available chlorides on the pore wall surfaces.

5. MODEL FOR CHLORIDE PENETRATION AND RETENTION IN CONCRETE

Simple computations, assuming concrete density of 2.2 g/cc, show that a concentration of 0.1% (eq. NaCl), will need to have a pore volume of 7.5% fully saturated with 3.3% salt solution (1.67% in case of 15% NaCl), and the required pore volume increases linearly with respect to chloride concentration, if the assumption that the NaCl does not react and is not deposited, is made. The possibility of the NaCl concentration in the pore water exceeding that of the outside solution can obviously be ruled out and since the solubility limit of NaCl is much higher than 15%, the possibility of deposition on account of super saturation of the pore water can also be ruled out. Further, since only C_3A content

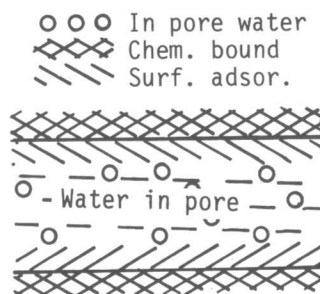


Fig. 6 Model for types of Cl^- in concrete

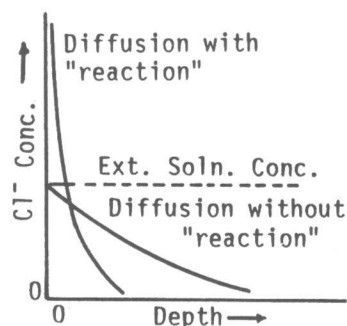


Fig. 7 Total Cl^- conc. vs. depth with/without "reaction" (Reference 5)

has been so far assumed to reflect the binding capacity (chem.) and through prolonged curing, it's complete hydration can be assumed, the possibility of chemical combination with cement, as is presently understood, can be taken to be excluded.

The facts cited above, leave us with only the following plausible scenario to explain the high chloride concentrations observed not only in this study but also by others (e.g. Ref.1): the chlorides available at a given location in hardened concrete are partly adsorbed by the walls of the pores and thus constitute a third form of chlorides in concrete in addition to the two discussed in section 1 above. This has been schematically represented in figure 6. The adsorption process lowers the Cl^- concentration in the pore water and leads to more chlorides being drawn in from the outside because of the concentration gradient that arises. Another way of looking at this phenomenon could be to visualize chloride incorporation into the C-S-H gel⁽⁴⁾, etc.. The model put forward here is in line with that put forward earlier⁽⁵⁾ provided, the word "reaction" (Fig. 7) is interpreted as a combination of chemical binding and surface adsorption. However, a direct estimation of the chlorides in the different states (Fig. 6) is extremely difficult except through indirect means as suggested here : the difference between the measured total chloride content (A) and the binding capacity of the C_3A (B) and in the pore solution (C), i.e., (A-B-C) be taken as trapped by the silicates, etc.. This aspect of chloride penetration is however, of considerable interest and tremendous practical importance in determining the relative chloride binding capacity of different cements.

6. CONCLUSIONS

- 1) The chlorides penetrating into concrete with permeating water lead to higher and deeper contamination of the concrete. And therefore, the chloride penetration along with the water is perhaps more important than chloride penetration occurring under concentration alone.
- 2) Concrete apparently maintains some sort of binding ability to hold penetrating chlorides even after sufficient curing and hydration. This mechanism has been modeled as a surface adsorption process in this study. The experimental values obtained for the chloride concentrations are too high to be accounted for if the pore walls are assumed to be inert.

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