



THE EFFECT OF CEMENT TYPE ON THE DIFFUSION OF CHLORIDE

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ABSTRACT

Chloride diffusion measurements have been made on cement paste samples of three cement types and with three water/cement ratios. The effects of curing time and temperature have also been investigated. The results indicate that w/c ratio has the greatest influence on chloride diffusion rates and that the C_3A content of the paste is not as important as has previously been assumed.

Keywords: Chloride, diffusion, reinforcement corrosion, water/cement ratio, cement type, flyash ash cement, temperature.

1. **INTRODUCTION**

The importance of chloride diffusion and penetration in concrete has been dramatically highlighted in recent years by the astronomical costs of highway bridge repair in North America and Europe resulting from reinforcement corrosion in these structures due to attack of the steel by deicing salts. Chloride induced corrosion of reinforcing steel is also a significant problem in those countries, particularly in the Middle East, where fresh mixing water and chloride-free aggregate are in short supply. Although the diffusion rate of chloride in the cement paste phase of concrete has previously been determined by

several investigators /1-6/, the relative importance of cement type, water/cement ratio and hardening conditions had not been determined. With the increased use of blended cements, it was felt that such an investigation was relevant and it has, therefore, been included as part of a European Common Market COST 502 Project.

3. EXPERIMENTAL PROCEDURE

Three cements, namely low alkali, sulphate resistant Portland cement (SRPC), rapid hardening Portland cement (RHPC) and flyash Portland cement (Standard) were supplied by the Aalborg Portland Cement Fabrik together with the analyses, given in Table I.

Preliminary measurements were made on paste samples of each cement with water/cement (w/c) ratios of 0.40 and 0.60. The pastes were cast into cylindrical tubes 45 mm ϕ x 400 mm and were rotated for 24 hrs. to prevent bleeding and were demoulded after a further 24 hrs. The rods of paste were then kept under water for either 28 or 90 days.

TABLE I

Composition, in wt. %, and Blaine surface area, in m^2/kg , of the cements.

	Standard Clinker Analysis	RHPC Analysis	SRPC Cement Analysis
C ₃ S	58		49
C ₂ S	21		33
C ₃ A	8		2
C ₄ AF	8		9
CaSO ₄	0		5.5
Free CaO	1		0.7
Flyash addition	22	3	0
Gypsum addition	4.5	4.5	0
Surface area	440	400	300

After the appropriate curing period, slices, approximately 3 mm thick, were cut from the paste cylinders and were glued with polyurethane glue to the neck of a plastic bottle in the bottom of which a hole was cut. The bottles were then inverted and partially filled

with a half saturated Ca(OH)_2 solution. As illustrated in Fig. 1, the inverted bottles were then immersed to the level of the solution inside the bottle in a half saturated solution of Ca(OH)_2 also containing 1 M NaCl. Chloride ions were thus able to diffuse through the paste into the solution inside the bottles.

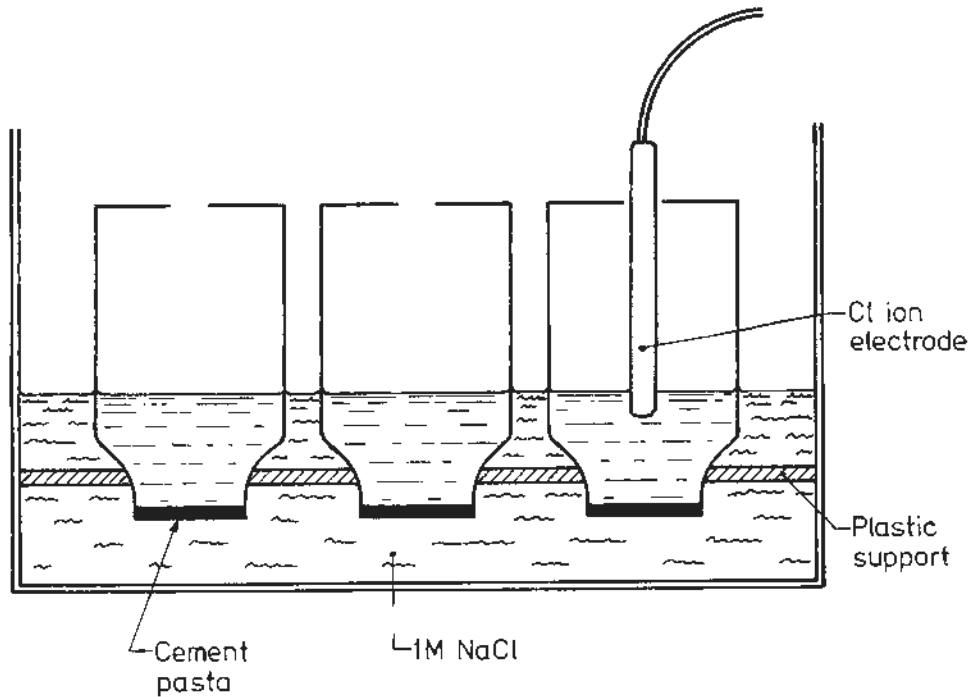


Fig. 1. Schematic drawing of the experimental arrangement

Three samples of each cement type and each w/c ratio were set up as described above and held at 30°C . The chloride content of the solution in each bottle was determined periodically using a chloride selective electrode.

Two sources of error were exposed by this experiment. The first was due to instability of the electrode and, as these electrodes have a finite lifetime, it was replaced with new electrode in subsequent tests. The second source of error was the increase in the ionic strength of the solutions during the course of the experiment, which calculations showed to be outside the tolerable range of the electrode.

The experiment was, therefore, repeated using the casting and curing procedure described above and cement pastes with w/c ratios of 0.40, 0.50 and 0.60. In order to maintain a relatively constant ionic strength of the solutions, NaNO_3 was added to the solutions in the bottles, to the chloride solution and to the calibration solutions, to a concentration of 0.1 M.

The samples were then set up as before at 30°C and, in addition, samples of each cement type and w/c = 0.50 were measured at 20° and 50°C . Three samples were measured for each combination of cement type, w/c ratio, hardening time and temperature. The chloride ion content of each bottle was determined daily using the new chloride selective electrode and periodical checks were also made by titration with AgNO_3 according to the Danish Standard DS239 and with "Quantab" strips.

3. RESULTS

Typical plots of chloride ion concentration of the solution in the bottle versus time are shown in Figs. 2 and 3. The slope of the linear portion of this curve corresponds to the number of ions diffusing through the cement paste slice per unit time under steady state conditions. It does not take into account those Cl^- ions entering the cement and becoming chemically bound, for example, as Friedel salt, or being physically or chemically adsorbed on the cement gel. This diffusion rate can, therefore, be used to determine the effective diffusion coefficient for Cl^- through the paste using Fick's First Law:

$$J = -D (dc/dx)$$

where J is the flux of ions, i.e. the number of ions diffusing over unit area and through unit thickness of paste per unit time, D is the effective diffusion coefficient and dc/dx is the chloride concentration gradient through the paste slice.

Using this relationship, effective diffusion coefficients were calculated from the concentration/time data. The results for the preliminary measurements are given in Table II and for the subsequent measurements in Table III.

TABLE II

Effective diffusion coefficients for cement pastes, $10^{-13} \text{ m}^2/\text{s}$, obtained from the preliminary experiments at 30°C .

w/c	28 days curing		90 days curing	
	0.40	0.60	0.40	0.60
Standard	27	107	3.1	26
RHPC	44	183	35	215
SRPC	76	212	96	286

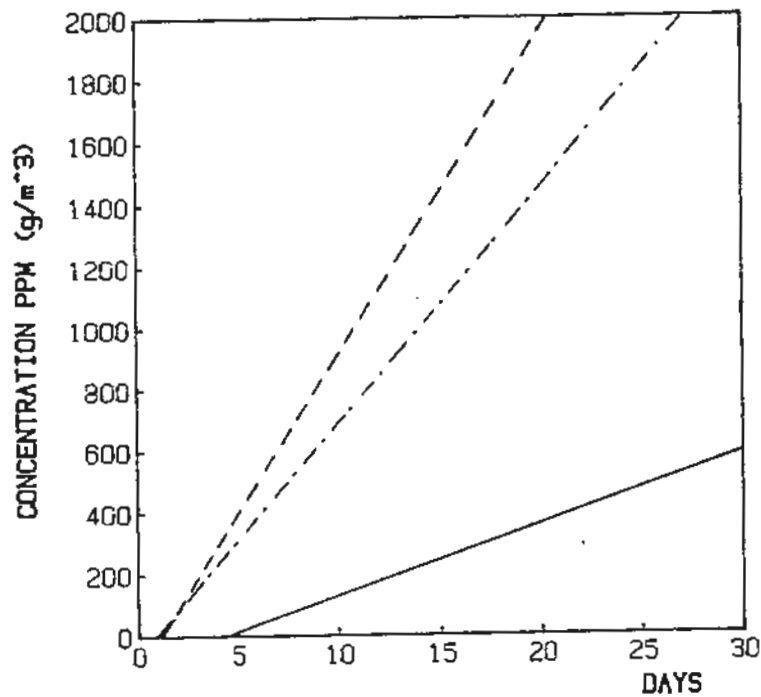


Fig. 2. The effect of cement type on chloride diffusion at 30°C through cement paste of $w/c = 0.50$ cured for 90 days. Standard:—
RHPC: - · - · -
SRPC: - - -

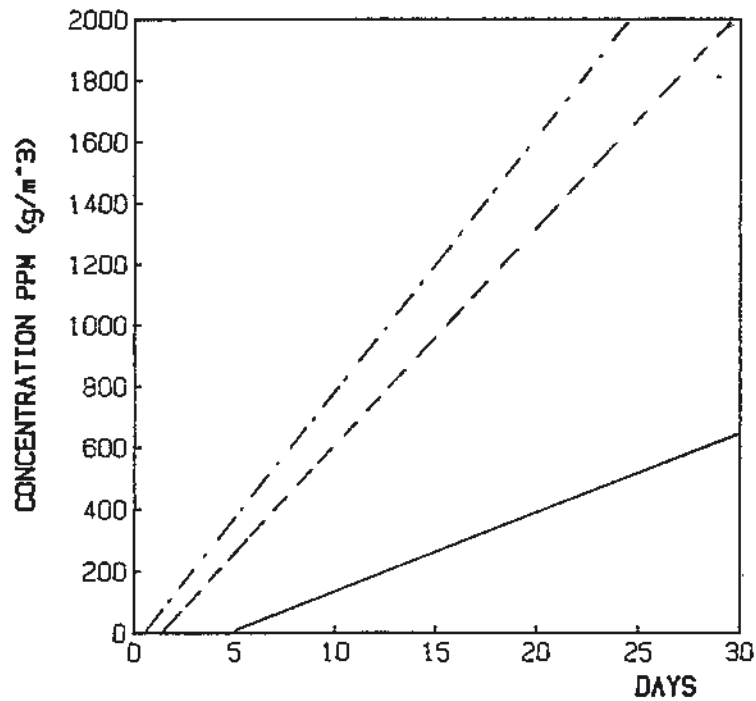


Fig. 3. The effect of w/c ratio on chloride diffusion at 30°C through Standard cement paste cured for 28 days. w/c = 0.40 ——— ; w/c = 0.50 - - - - - ; w/c = 0.60 - · - · - ·

TABLE III

Effective diffusion coefficients for cement pastes, $10^{-3}m^2/s$.

T / w/c	28 days curing			90 days curing		
	0.40	0.50	0.60	0.40	0.50	0.60
Standard 20°C	-	92	-	-	29	-
30°C	41	116	139	5.8	37	88
50°C	-	137	-	-	66	-
RHPC 20°C	-	122	-	-	100	-
30°C	67	132	263	45	125	257
50°C	-	289	-	-	284	-
SRPC 20°C	-	151	-	-	140	-
30°C	106	193	279	83	171	160
50°C	-	370	-	-	388	-

The activation energy, E_a , for the diffusion process is given by the relationship:

$$D = D_0 \exp(-E_a/RT)$$

where D_0 is the diffusivity, R is the universal gas constant and T is the Kelvin temperature. The activation energy can be determined from the slope of the plot of $\log D$ vs. $1/T$. The data from Table III have been plotted in this form and the calculated values of E_a are given in Table IV.

TABLE IV

The activation energies for chloride diffusion through cement pastes with a w/c ratio of 0.50. The values are given in kJ/mol.

	28 days curing	90 days curing
Standard	10	23
SRPC	24	28
RHPC	24	28

4. DISCUSSION OF THE RESULTS

The results of the preliminary experiment have been included in this report in order to demonstrate that the absolute values of diffusion coefficient can be affected by the actual measuring procedure, in this case the presence of the NaNO_3 and the use of a new and more stable measuring electrode. Furthermore, some of the difference between the data in Tables II and III must be attributed to the fact the samples came from different mixes made at different times of the year and by different personnel. It should be noted that the scatter in the diffusion coefficients within each set of three "identical" samples was between 5 and 20% for the data in Table II and between 1 and 9% for the data in Table III.

Despite the differences in absolute values, however, the trends with respect to cement type and w/c ratio are similar for the two sets of data and these trends are, therefore, only discussed below with reference to the data in Table III.

Diffusion through cement paste

The rate at which chloride ions enter and diffuse through cement paste is a complex function of the composition, structure and fineness of the paste. There has been considerable discussion in the literature concerning the role of C_3A in chemically binding chloride ions, thereby removing them from the pore solution/7-9/. In addition, chloride ions can become bound in the gel phase either chemically or by being physically adsorbed on the gel surface. This latter effect will be strongly influenced by the fineness of the cement as this defines the surface area available for adsorption. The contribution of these binding effects might be assumed to be greatest at the beginning of the experiment and to decrease rapidly as the binding capacity of the cement becomes saturated. However, this is not entirely true because the binding capacity must follow the laws of phase equilibria and must be a function of the concentration of chloride present. Nevertheless, the results suggest that once the diffusion has reached "steady state", binding effects are not dominant and it is the structure of the paste pore system which controls the diffusion rate.

Effect of Cement Type

For all sets of data, the Standard cement paste exhibits the lowest diffusion rate for chlorides while the SRPC exhibits the highest. The RHPC lies between these two but closer to the SRPC than to the Standard. Since RHPC paste has the highest C_3A content of the three types, chemical binding of the chloride by the C_3A cannot be considered as the major cause of the differences in diffusion coefficients. The fineness of the cements, on the other hand, is in the same ranking order as the diffusion coefficients, i.e. SRPC has the coarsest structure and the highest diffusion rate, etc.

For the Standard cement, which contains 22% flyash, there is a second factor contributing to the fineness of the paste structure: as proposed by Bakker /10/ the CSH phase in unblended cements forms in close proximity to the clinker particles whereas the presence of flyash leads to production of CSH phase in the interstices between the particles, effectively refining the porosity. It is felt by the current authors that this, rather than the chemistry of the system, is the major reason for the low diffusion rates in the Standard paste.

Effect of w/c ratio

For all three types of cement, the diffusion rate increases with increasing w/c ratio as expected. It is important to note, however, that the effect of water cement ratio is greater than the effect of cement type: for both hardening times, diffusion through Standard cement with w/c = 0.60 is greater than that through RHPC or SRPC with w/c = 0.40.

Effect of curing time

The effect of increased curing time is negligible for RHPC cement paste which, as its name suggests hardens rapidly and involves only the clinker reaction. The hardening of SRPC paste also involves only the clinker reaction and the samples showed only a slight decrease in diffusion coefficient with increase in curing time, again compatible with its slightly slower hardening rate. The hardening of Standard paste, on the other hand involves both the clinker reaction and a pozzolanic reaction and, as indicated by resistivity measurements in these materials /11/ hardening of Standard paste is considerably slower than in the other two cements. This slow hardening reaction is reflected in the significant decrease in diffusion coefficients with curing time.

Effect of temperature

The diffusion coefficients increased with increasing temperature for all three cement types and the activation energies for diffusion through RHPC and SRPC were identical within the accuracy of the measurements. The activation energy for Standard cement, however, was lower indicating that temperature has less influence on the diffusion process in Standard paste than in RHPC or SRPC pastes. This observation may be explained in terms of the hardening rates and processes in the three cements.

It has been shown the hardening of unblended cements at elevated temperature leads to a coarser structure /10/. Thus, if the RHPC and SRPC samples were not fully hardened when exposed to chlorides at high temperatures the increased effective diffusion might be a combination of the coarsening effect and the inherent increased mobility of the chloride ions. The observation above that the samples appeared to be nearly fully hardened after 28 days suggests that the mobility of the chloride ions is the dominant factor in this case.

For blended cements, such as Standard, the effect of curing at elevated temperatures is a refinement of the structure /10/ and this factor together with the fact that the samples were not fully cured prior to exposure to chlorides probably accounts for the lower activation energies. Note that E for Standard is significantly lower than that for RHPC and SRPC when the samples were exposed to chlorides and an elevated temperature when only 28 days old, whereas the difference was much smaller for 90 day old samples.

5. **SUMMARY AND CONCLUSIONS**

1. The absolute values of diffusion coefficient are dependent on the particular measuring procedure and can be expected to differ from one set of measurements to the next. However, the values are within the same order of magnitude and the trends in the effects of the variables investigated were similar for both sets of measurements made in this study.

2. The water/cement ratio has the greatest effect on diffusion of chloride, the higher w/c ratio allowing much faster passage of chloride ions.

3. It does not appear from these results that the C_3A content is as effective in reducing the chloride diffusion as is normally considered. Instead, it appears to be the fineness of the cement paste phase which plays the major role in determining chloride diffusion rates. The presence of flyash was found to be advantageous under all conditions investigated and its beneficial effects were attributed to the refinement of the pore structure by the pozzolanic reaction.

4. The effect of increasing temperature was to increase the diffusion rates but this effect was significantly less for the flyash cement paste than for the unblended cement pastes.

5. In contrast, an increased curing period had the greatest effect on the flyash cement, again attributable to the pozzolanic reaction.

6. **ACKNOWLEDGEMENTS**

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7. **REFERENCES**

1. R.Kondo, M.Satake and H.Ushiyama, "Diffusion of Various Ions in Hardened Portland Cement", Cement Ass. Japan, 28th. Gen. Mtg., Tokyo (1974).
2. C.L.Page, N.R.Short and A.El Tarras, "Diffusion of Chloride Ions in Hardened Cement Pastes", Cement and Concrete Research, **11**, 395 (1981).
3. R.Bakker, Ph.D. Thesis, "On the Cause of the Increased Resistance of Concrete made from Blast Furnace Cement to the Alkali-Silica Reaction and to Sulphate Corrosion", R.W.T.H., Aachen (1980).
4. K.Shigeru, T.Tagaki, S.Goto and M.Daimon, "Diffusion of Ions through Hardened Cement Paste of Various Cement", Cement Ass. Japan, Review (1983).
5. S.Goto and D.Roy, "Diffusion of Ions through Hardened Cement Pastes", Cement and Concrete Research, **11**, 751 (1981).
6. C.M.Preece, "Corrosion of Steel in Concrete", SKBF KBS Technical Report 82-19, Stockholm (1982).
7. W.Richarz, "Die Bindung von Chlorid bei der Zementerhärtung", Zement-Kalk-Gips, **10**, 447 (1969).
8. V.S.Ramachandran, R.C.Sealey and G.M.Palomark, "Free and Combined Chlorides in Hydrating Cement and Cement Compounds", Materiaux et Constructions **0025-5432**, 284 (1984).
9. J.Tritthart, "Bewehrungskorrosion - Zur Frage des Chloridbindevermögens von Zement", Zement-Kalk-Gips, **37**, 200 (1984).
10. R.Bakker, "Permeation of Blended Cement Concrete", Proc. CANMET/ACI 1st. Int.Conf. on the Use of Flyash, Silica Fume, Slag and Other Mineral Byproducts in Concrete, ACI Publ. SP-79, p.589 (1983).
11. I.L.H.Hansson and C.M.Hansson, "Ionic Conduction, Porosity and Pore Solution Composition of Cement Pastes", to be published.