



THE INFLUENCE OF CEMENT FINENESS ON CHLORIDE DIFFUSION AND CHLORIDE BINDING IN HARDENED CEMENT PASTE

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ABSTRACT

An investigation has been made of the influence of cement's specific surface area on the rate of chloride diffusion through and the degree of chloride binding in hardened cement paste prepared with low alkali sulphate resistant Portland cement, with and without flyash additions. While there is an observable effect of surface area for pastes with $w/c = 0.50$, there is negligible effect for pastes with $w/c = 0.42$ and for pastes containing 15% flyash and with $w/c = 0.39$.

KEY WORDS: cement fineness, chloride diffusion, chloride binding, porosity, sulphate resistant Portland cement, flyash.

I. INTRODUCTION

The most widespread cause of reinforcement corrosion in concrete is the presence of chloride ions in the cement paste pore solution. These ions break down the passive film on the steel surface which is formed in the highly alkaline pore solution and which otherwise prevents the steel from actively corroding. The breakdown of the film by chloride ions does not occur generally over the whole steel surface: instead the attack is very localised, probably occurring in the region of flaws in the film, and, thereby, creating galvanic cells in which the area of attack acts as anode, with high rates of corrosion, and the remaining passive steel is the cathode where the corrosion rate is negligible.

The results presented here are part of a larger investigation, the overall aim of which is to identify the various factors influencing the initiation of reinforcement corrosion by chlorides and the subsequent rates of corrosion. The investigation

is being conducted in collaboration with the Swedish Cement and Concrete Research Institute and the Technical University of Graz, Austria within the European Community COST 502 programme.

Previously reported results obtained within the investigation have shown that, contrary to earlier opinion, the content of aluminium phases in the cements cannot be the single overriding factor controlling the degree of chloride binding¹ or the rates of diffusion of chlorides through cement paste². For example, the data given in Table I show that the Danish ordinary Portland cement (OPC) contains considerably more tricalcium aluminate (C_3A) and tetracalcium aluminoferrite C_4AF than does the Danish Standard Cement (a blended cement with 23% flyash), yet the Standard cement can bind more chloride than can the OPC. Similarly, of the three commercial Danish cement types, low alkali sulphate resistant Portland cement (SRPC), rapid hardening Portland cement (RHPC) and the Standard cement, the Standard cement exhibited the lowest diffusion rates for chlorides and the SRPC exhibited the highest whereas it is the RHPC which has the highest content of C_3A and C_4AF .

TABLE I

The aluminium phase contents, the specific surface areas, the effective chloride diffusion coefficients, D , of 28 day old paste with $w/c = 0.50$ (from Ref. 2) and the chloride content of the pore solution of three month old pastes containing a total of 1% chloride by weight of the cement as NaCl and $w/c = 0.60$ (from Ref. 1).

Cement type:	OPC	SRPC	RHPC	Standard
C_3A , %	10.8	2.0	7.7	6.3
C_4AF , %	9.1	9.0	7.7	6.3
S , m^2/kg	300	300	400	440
D , $10^{-12} m^2/s$	n.d.	15.1	12.2	9.2
Cl^- , conc. g/l	12.3	17.7	n.d.	8.6

n.d. = not determined

In analysis of these results, however, it was noted that there is a qualitative correlation between both chloride binding and diffusion and the fineness (specific surface area) of the cement. SRPC traditionally has a coarser grain distribution than other Portland cements in order to minimise the heat development during hardening of massive structures and it was thought that this might also be one factor in its relatively inferior protection of steel against chloride attack. Thus, the purpose of the investigation reported here was to determine the influence of cement fineness on the chloride diffusion rates and degree of chloride binding in pastes prepared with SRPC and SRPC/flyash blends.

II. EXPERIMENTAL PROCEDURE

Specimen Preparation

Samples of SRPC milled to finenesses equivalent to Blaine specific surface areas of 300, 376 and 444 m²/kg and the flyash were supplied by the Aalborg Portland Cement-Fabrik. For diffusion measurements, cement paste samples were prepared with water/cement ratios (w/c) of 0.50 and 0.42. Cement/flyash pastes were mixed with 15% flyash and a water/binder (w/b) ratio of 0.39. In order to determine the degree of chloride binding, a second set of pastes of each of these compositions was prepared with additions of chloride (as NaCl) to the mixing water in concentrations equivalent to 1% by weight of the cement or cement + flyash.

The pastes were cast into 45 mm ø cylindrical moulds and were rotated for 24 hours to minimise bleeding and were subsequently stored in 100% RH atmosphere at laboratory temperature (approx. 20°C).

No difficulties were encountered in mixing the SRPC paste with a w/c = 0.50 or any of the samples containing flyash. On the other hand, samples with w/c = 0.42 proved to be more problematic: the cement with Blaine fineness of 444 m²/kg was difficult to blend and the hardened paste was found to contain clumps of unblended and unhydrated cement. Because of this, new samples were prepared using additions of 0.5% by weight of the cement of a dispersing agent. In this case, there was no difficulty with the finely ground cement but bleeding was encountered in pastes prepared using the coarse cement with the dispersing agent.

Diffusion measurements

After 28 days, the pastes without chloride were sectioned into 3mm slices and each slice was glued to the neck of a plastic bottle. As illustrated in Fig. 1, the bottles were inverted, set on a rack in a tank containing a 1 M NaCl solution saturated in $\text{Ca}(\text{OH})_2$, and filled to the level of the tank solution with a half saturated $\text{Ca}(\text{OH})_2$ solution. Four to six samples of each cement mix was tested.

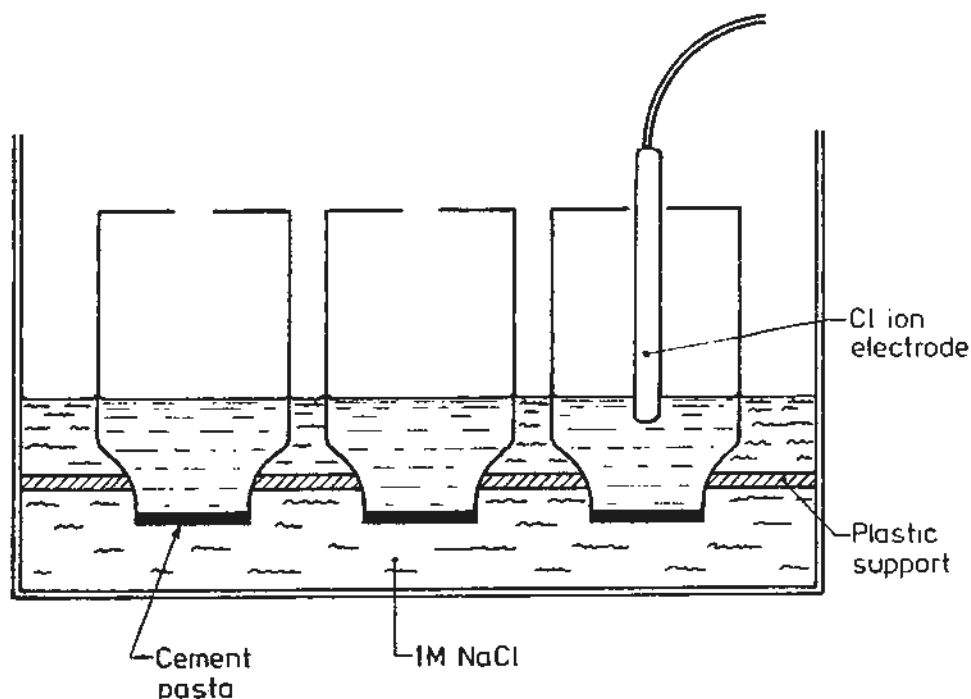


Fig.1. Experimental set-up for measurement of chloride ion diffusion through the cement paste.

The amount of chloride diffusing through the paste slices was determined by periodically measuring the chloride content of the solution in the bottles using a chloride ion selective electrode.

Chloride Binding Measurements

In order to determine the degree of chloride binding, the pore solution chloride content and the total free water content were determined for the pastes containing NaCl after three months curing in 100% RH.

To determine the pore solution chloride content, the solution was

expressed from crushed samples of each paste using the press illustrated in Fig. 2. The hydroxyl ion content of the solution was determined by titration against 0.1N HCl and the pH calculated from this value. The chloride ion content was determined by potentiometric titration with 0.01N AgNO₃. The pore solution from two samples of each mix was expressed and analysed. The data given in Section III are the average of those from the two samples.

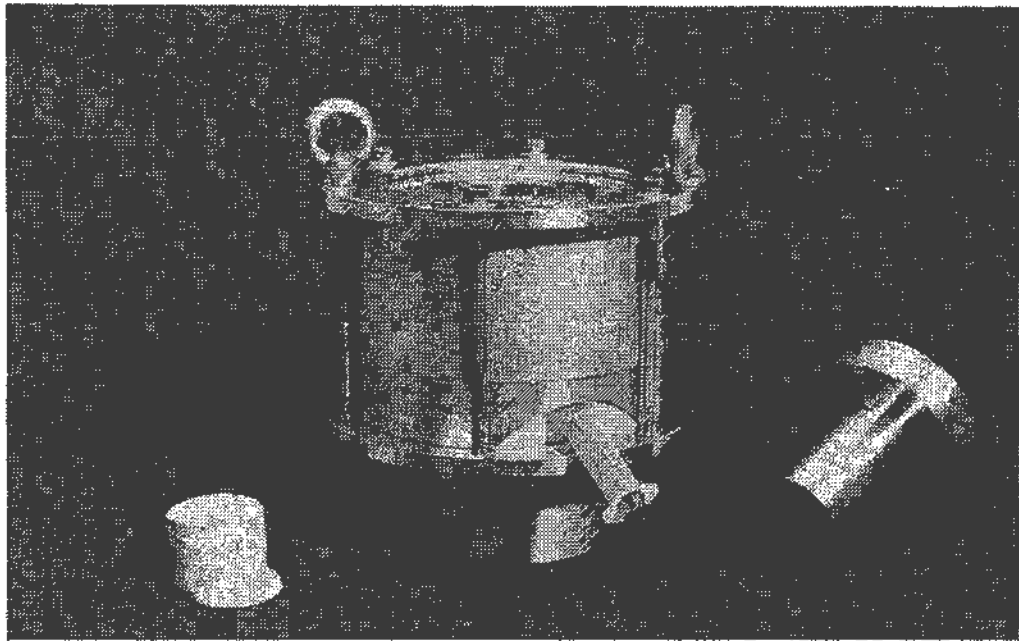


Fig. 2. Cylinder and piston used for expressing pore solution from a cement paste sample such as that shown on the left of the figure. The pore solution is collected in the syringe and carbonation is, thereby, minimised.

The free water contents were determined by drying weighed samples at 105°C and reweighing.

The total amount of chloride in solution was calculated from these two measurements assuming that the amount of water used for total hydration is 25% by weight of cement and, by subtraction from the known amount of added chloride, the total bound chloride was calculated.

Pore Size Distribution

The pore size distribution of samples of each of the pastes

without chloride additions and two of those with chlorides was determined by mercury porosimetry within the porosity range from 1.8 nm to 7 μ m. The measurements were made on samples which were crushed and then dried for two hours under a vacuum of 10^{-4} torr.

III. RESULTS AND DISCUSSION

Chloride Diffusion Rates

Typical data for the variation with time of chloride concentration in the initially chloride-free solution in the bottles are given in Figs. 3 and 4. Typical scatter within one set of data is illustrated in Fig. 3 where all the data for six samples of the same paste blend all fall within the shaded region. To illustrate the variation in chloride diffusion rates with cement blend, the data for the three blends with the same specific surface area are plotted in Fig. 4.

The slope of the linear portion of these curves corresponds to the number of ions diffusing through the cement paste per unit time under steady state conditions. It does not take into account those Cl^- ions entering the cement and becoming bound, for example, as Friedel salt, or being physically or chemically adsorbed on or trapped in the cement gel. The effective diffusion coefficients for Cl^- through the pastes, given in Table II, have been calculated from these diffusion rates using Fick's first law:

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

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

The data for SRPC pastes with $w/c = 0.50$ are plotted versus specific surface area in Fig. 5 together with the data from Ref. 2 given in Table I. There is a clear, if not very pronounced, trend of decreasing diffusion coefficient with increasing specific surface area for both sets of data.

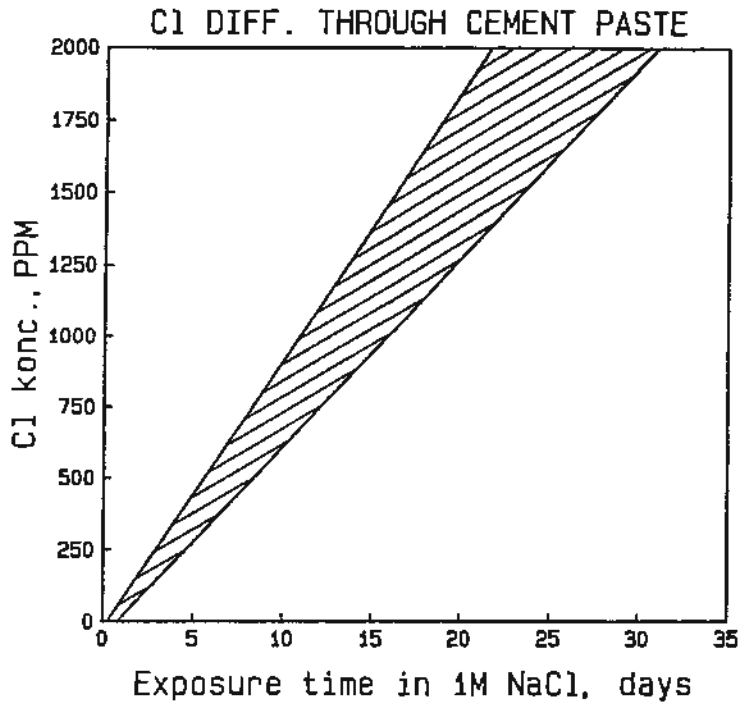


Fig. 3. The variation with time of the chloride concentration. The data for six samples of SRPC + 0.5% disp. agent paste with w/c = 0.42 all within the shaded area.

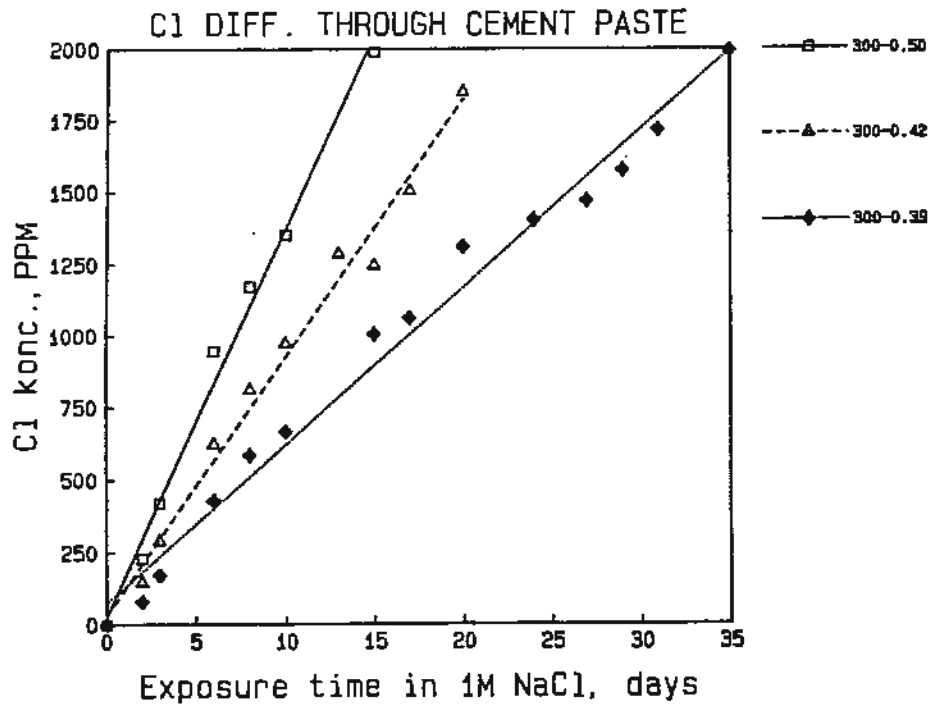


Fig. 4. The chloride diffusion through cement paste with specific surface area of $300 \text{ m}^2/\text{kg}$. □—□ SRPC w/c = 0.50; Δ----Δ SRPC + 5% disp. agent, w/c = 0.42; ...◆.....◆ SRPC + 15% flyash, w/b = 0.39

TABLE II

Effective chloride diffusion coefficients for 28 day old sulphate resistant Portlant cement paste with and without flyash at 20°C, $m^2/s \cdot 10^{12}$. The data are the average values for four to six samples of the same composition and their standard deviations.

Binder	Water/binder	Cement specific surface area, m^2/kg					
		300		376		444	
SRPC	0.50	17.5	5.2	14.7	0.6	10.9	2.8
SRPC	0.42	10.8	2.3	9.9	2.1	16.7	8.3
SRPC + 0.5% disp.	0.42	8.8	1.5	12.4	2.2	11.2	1.4
SRPC + 15% flyash	0.39	7.3	1.5	10.8	2.1	8.1	2.1

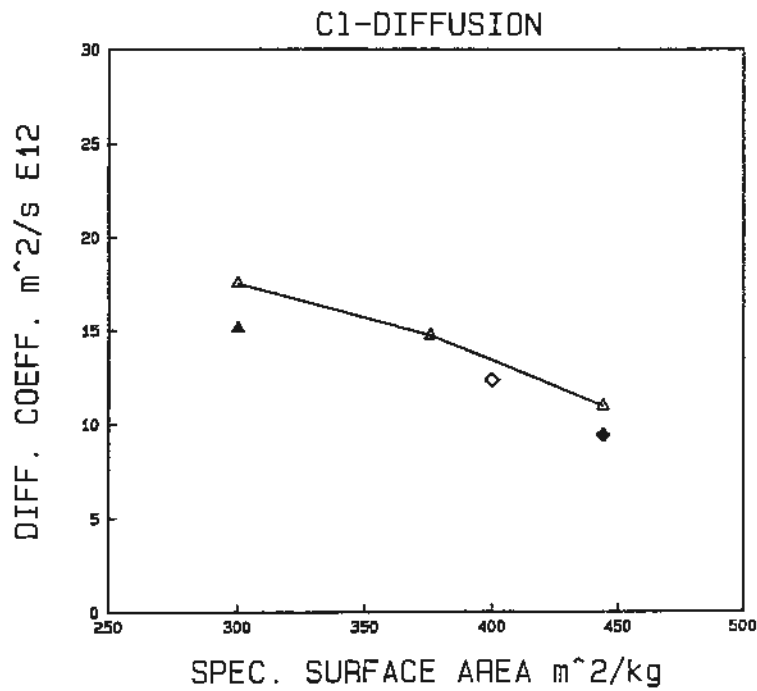


Fig. 5. The effective diffusion coefficient for pastes with w/c = 0.50 as a function of specific surface area. Δ — Δ — Δ SRPC from the present experiments; \blacktriangle SRPC, \diamond RHPC; \blacklozenge Standard cements from Ref. 2.

This trend is not, however, observed for pastes with the lower, more realistic, water/cement ratios, as shown in Fig. 6. In this figure, the data point marked "A" corresponding to the paste with $S = 300 \text{ m}^2/\text{kg}$, $w/c = 0.42$ and containing the dispersing agent is probably unrealistically low because the bleeding in this paste, described earlier, is likely to have resulted in an effective w/c ratio in the hardened samples lower than 0.42. Similarly, the data point marked "B" is almost certainly too high because presence of the unhydrated clumps of cement, also described earlier, would mean that the remaining paste has a higher effective w/c ratio than the nominal 0.42. Furthermore, it is possible that the chlorides can be transported more rapidly through the unhydrated clumps than through the matrix. If these two data points are ignored and the remaining points taken to be the correct ones, the diffusion coefficients for chloride through SRPC samples of $w/c = 0.42$ are seen to be independent of the fineness of the cement. A similar conclusion can be made for the pastes containing flyash.

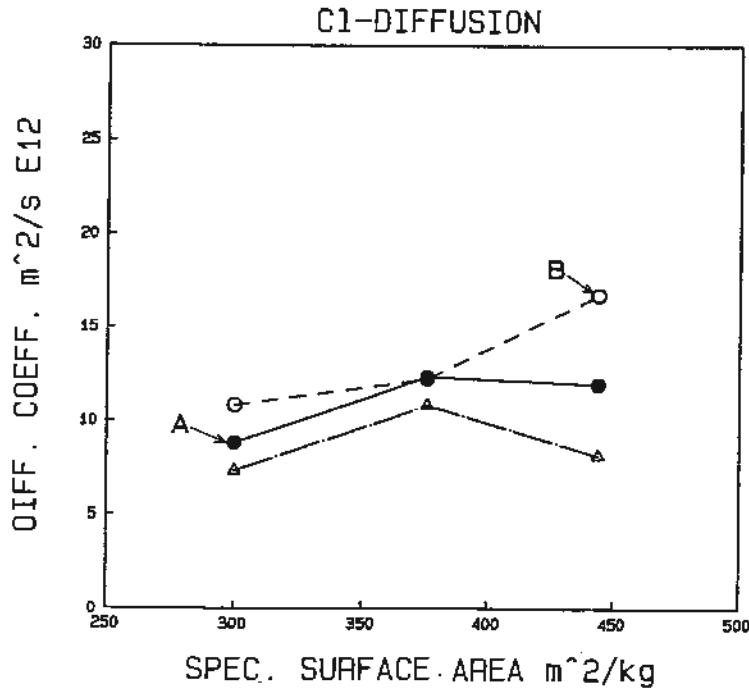


Fig. 6. The effective chloride diffusions coefficients as a function of specific surface area.

- SRPC, $w/c = 0.42$
- SRPC + 0.5% dispersing agent, $w/c = 0.42$
- △—△—△ SRPC + 15% flyash, $w/b = 0.39$

It appears from Fig. 6 that flyash has only a minor influence on the diffusion of chlorides. This is in agreement with earlier observations on 28 day old Standard cement (Table I and Fig. 5). However, in the previous work², it was observed that if samples were first exposed to the chloride solution after three months' hardening, there was a considerable increase in resistance to Cl^- diffusion of the Standard cement relative to both SRPC and RHPC. Similarly, Page et al.,³ have shown that, for 60 day old pastes, additions of 30% flyash to OPC reduces the chloride diffusion coefficient by a factor of approximately 3. It is highly likely, therefore, that a more significant effect of the flyash would be observed in the blended cement in the present experiment if the Pozzolanic reaction were given more time to develop before the paste was exposed to the chlorides.

Chloride Binding

The results of the pore solution analysis are given in Table III and the chloride contents of the pore solutions are plotted as a function of the cement's specific surface area in Fig. 7. The lower values of both pH and Cl^- content in the pastes with $w/c = 0.50$ relative to the other cements are due to an effective dil-

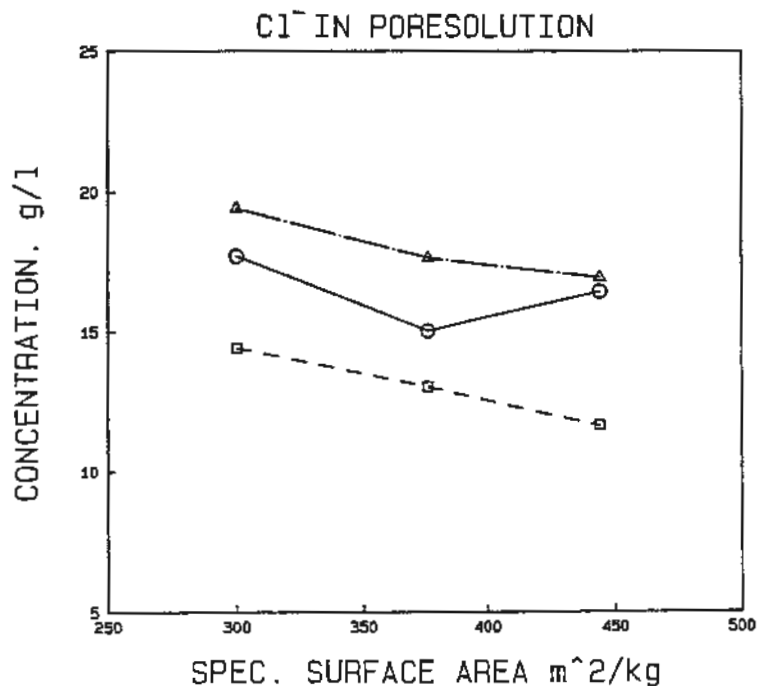


Fig.7. The pore solution chloride content of three month old cement pastes as a function of specific surface area.

- △--△--△-- SRPC w/c = 0.50;
- SRPC + 0.5% dispersing agent, w/c = 0.42
- SRPC + 15% flyash, w/b = 0.39

ution by the higher water content. It should also be noted that the Pozzolanic reaction in the flyash cements does not cause a significant drop in pH.

TABLE III

Pore solution analysis of three month old cement pastes with and without additions of chloride as NaCl. The total free (evaporable) water content is given as weight % of the hardened dry paste and the free (dissolved) chloride content as % of the total added chloride.

Flyash %	w/c	Disp. agent%	S	Total Cl ⁻ %	OH ⁻ mole	pH	Cl ⁻ g/l	Free water	Free Cl ⁻
-	0.50	-	300	1.0	0.213	13.33	14.4	35.8	49
-	0.50	-	376	1.0	0.234	13.37	13.0	32.9	44
-	0.50	-	444	1.0	0.245	13.39	11.6	33.4	39
-	0.42	-	300	1.0	0.213	13.33	17.9	26.7	48
-	0.42	-	376	1.0	0.257	13.41	17.6	26.6	47
-	0.42	-	444	1.0	0.257	13.41	16.9	26.4	45
-	0.42	0.5	300	1.0	0.275	13.44	19.4	26.3	51
-	0.42	0.5	376	1.0	0.295	13.47	17.6	26.5	46
-	0.42	0.5	444	1.0	0.269	13.43	15.8	26.8	42
15	0.39	-	300	1.0	0.263	13.42	17.7	30.4	50
15	0.39	-	376	1.0	0.251	13.40	15.0	27.4	42
15	0.39	-	444	1.0	0.257	13.41	16.4	26.0	46
-	0.50	-	300	-	0.141	13.15	-	32.2	-
-	0.50	-	376	-	0.144	13.16	-	32.6	-
-	0.50	-	444	-	0.129	13.11	-	32.1	-
-	0.42	-	300	-	0.162	13.21	-	25.1	-
-	0.42	-	376	-	0.178	13.25	-	26.4	-
-	0.42	-	444	-	0.186	13.27	-	26.5	-
15	0.39	-	300	-	0.190	13.28	-	25.1	-
15	0.39	-	376	-	0.174	13.24	-	23.7	-
15	0.39	-	444	-	0.195	13.29	-	25.1	-

Porosity and pore size distribution

The results of the mercury porosimetry measurements are given Figs. 8 and 9. It should be noted that only those pores with diameters smaller than 7 μm and larger than 1.8 nm have been measured and the measured pore volume is, therefore, considerable smaller than that determined by drying measurements and given in Table III. It must also be emphasised that these data were

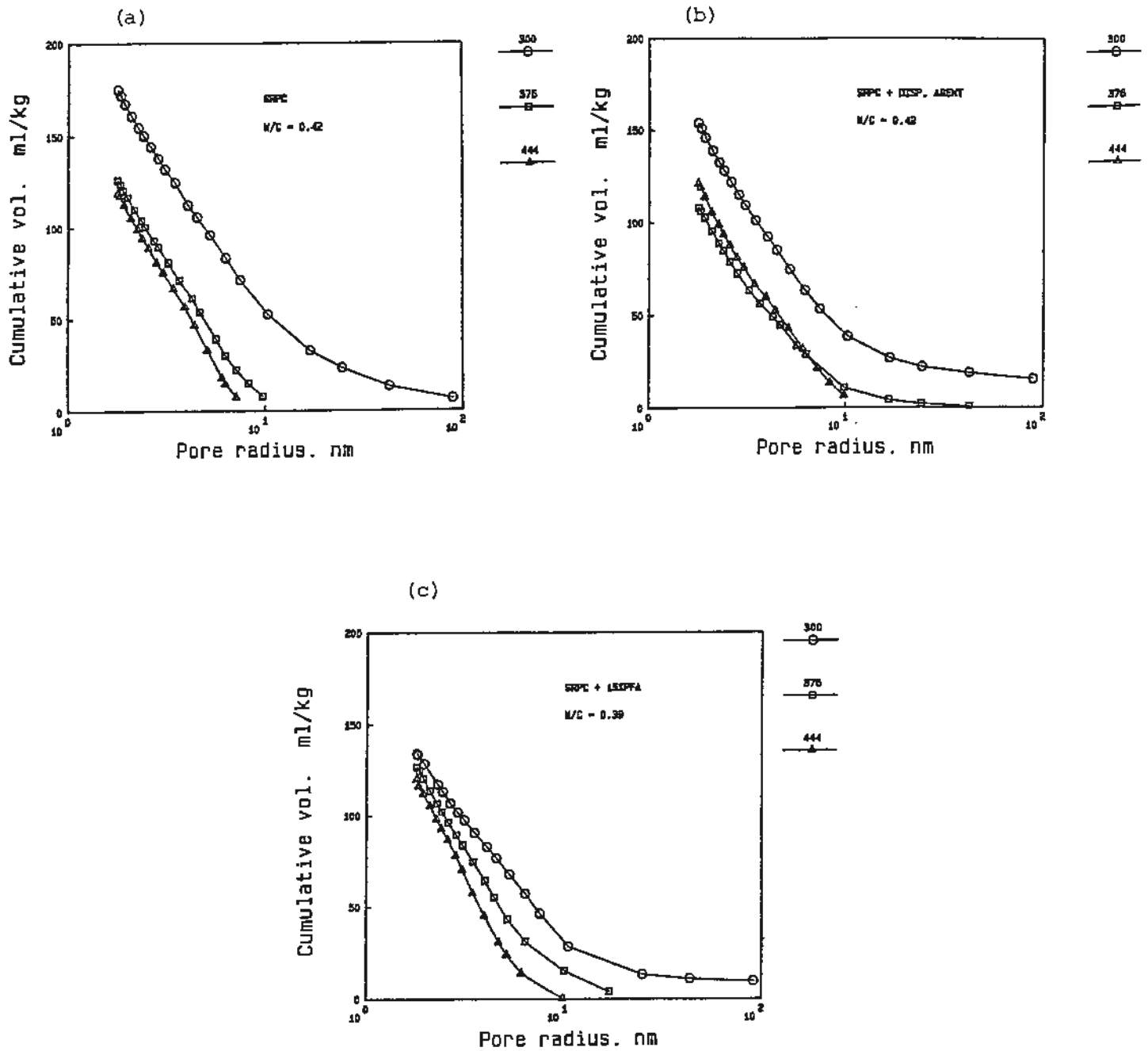


Fig. 8. The pores size distribution in vacuum-dried cement pastes determined by mercury porosimetry. (a) SRPC w/c 0.42; (b) SRPC + 0.5% disp. agent, w/c = 0.42; (c) SRPC + 15% flyash, w/b = 0.39.

obtained for samples which were dried under vacuum and that the results will be different for samples of the same materials dried under different conditions. Moreover, there is a degree of uncertainty in the data for pores smaller than approx. 6 nm due to electrical noise in the measuring system.

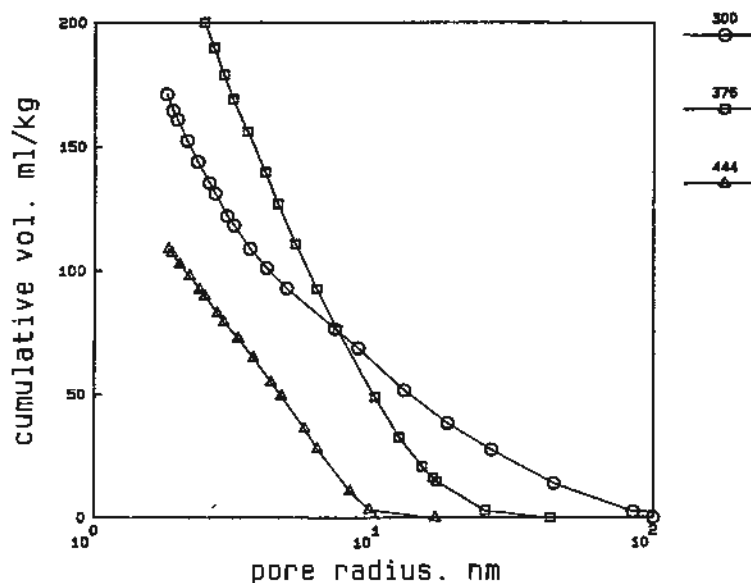


Fig. 9. the pore size distribution in vacuum-dried SRPC cement paste samples with $w/c = 0.50$, determined by mercury porosimetry.

It can be seen from Fig. 8 that, for samples with $w/c = 0.42$, with or without dispersing agent, those with specific surface area of $300 \text{ m}^2/\text{kg}$ have a significantly coarser pore size distribution than have the samples with $S = 376$ or $444 \text{ m}^2/\text{kg}$ while there is little observable difference in the data for the two latter sets of samples.

For the samples with $w/c = 0.50$, the observed variation in chloride diffusion rates can only be explained if it is assumed that diffusion occurs predominantly through the larger capillary pores: for pore radii $> 7 \text{ nm}$, there is an increase in pore volume with decreasing specific surface area as expected. The reasons for the cross-over of the curves for $S = 300$ and $S = 376$ at pore radii of 7 nm is not clear. This trend was confirmed by repeated measurements on different samples of the same blend and is, therefore, considered to be a real effect which requires further investigation.

For the samples containing flyash, on the other hand, there is a

smaller total variation in the data but there is a definite observable increase in porosity with decreasing fineness at all pore sizes.

Potential consequences of the observed variations in chloride diffusion rates and chloride binding with cement fineness

The cement's fineness can potentially have several effects on the hardened paste. Firstly, the higher surface area will result in a faster, more complete hydration of the cement which could, in fact, lead to a more dense gel and a more open capillary pore structure between the hydrated gel "particles". Thus the Cl^- ions could experience wider pores but a longer, more tortuous route which could account for the lack of any really significant trend in diffusion coefficient with surface area for the pastes with a low water/binder ratio.

What is not so easily explained, however, is the lack of any influence of water/binder ratio for pastes with a high specific surface area.

The second potential effect of a higher specific surface areas is a faster chemical reaction with any chlorides blended into the mix. The third possible effect is that it will allow a greater degree of chemical or physical adsorption of chlorides either present in the blend or penetrating from the environment.

While the observed effect of the cement's fineness is not very significant on either the diffusion rates of chloride or the degree of binding, it is worthwhile considering whether these two minor effects could have a more significant influence in combination, for example, on the time for sufficient chloride to penetrate from the environment to initiate corrosion of embedded steel.

The time required to initiate corrosion of steel embedded in cement paste prepared with the "best" and the "worst" blends has been calculated from their diffusion coefficients and a knowledge of the proportion of total chloride which remains dissolved in the pore solution. Two cases have been considered: one in which the pastes have the same total chloride content (1% by weight of the cement) at the surface and the second in which they have the same free chloride content (1.4%) in the pore solution at the surface.

The following assumptions have been made (i) the cover is 50 mm; (ii) the samples are water saturated; (iii) that the amount of water necessary to fully hydrate cement is equal to 25% of the cement by weight; (iv) initiation of corrosion requires a total chloride content of 0.35% by weight of the cement of which 20% is assumed to be freely dissolved in the solution. This last assumption is made on the basis of practical measurements⁴ and the observation that the lower the total chloride content, the higher the proportion which is bound. The results are given in Table IV.

TABLE IV

The time, t_i , to initiate corrosion for samples with a constant total chloride content.

Blend	S, m ² /kg	water/binder	t_i , yrs.	
SRPC	300	0.50	2.5	} Constant total Cl ⁻
SRPC + 0.5% disp.	444	0.42	3.9	
SRPC + 15% flyash	444	0,39	5,5	
SRPC	300	0.50	2.5	} Constant Cl ⁻ in solution
SRPC + 0.5% disp	444	0.42	4.9	
SRPC + 15% flyash	444	0,39	8,1	

It is probable that, in practice, the difference between the times to initiate corrosion would be greater than those shown in Table IV because the proportion of the total chloride at the steel interface has been assumed to be the same in each case and this will not be the case in practice. The differences should, therefore, be regarded as conservative.

IV. SUMMARY OF RESULTS AND CONCLUSIONS

1. For SRPC pastes with w/c = 0.50, the effective diffusion coefficient for chloride ions can be reduced by approx. 38% by increasing the specific surface area from 300 to 444 m/kg.
2. For SRPC pastes with w/c = 0.42, there is no observable effect of the cement's fineness on the effective diffusion coefficient for chloride ions.
3. Additions of 15% flyash to the cement gave a minor reduction

in effective chloride diffusion coefficient when samples are exposed to chlorides after 28 days. However, on the basis of previous results, it is expected that there would be a greater effect of flyash had the samples been allowed to mature longer before exposure to chlorides.

4. For SRPC pastes with a specific surface area, S , of 444 m²/kg there is no observable effect of water/cement ratio.

5. There is little difference in pore size distribution for samples with $w/c = 0.42$ and S of 376 or 444 but those with $S = 300$ show a significantly higher degree of porosity.

6. For samples with $w/c = 0.50$, the pore size distribution curves for $S = 376$ and $S = 300$ cross at pore radii of approx. 7 nm. The reason for this is, as yet, unclear. For larger pore sizes, there is a general increase in porosity with specific surface area which suggests that it is the larger pores which are responsible for chloride diffusion.

7. There is a small but consistent trend of higher porosity with lower specific surface area for samples containing flyash.

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