Pergamon

Cement and Concrete Research, Vol. 25, No. 8, pp. 1667-1678, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00163-8

DIFFUSION OF CHLORIDE IONS IN LIMESTONE FILLER BLENDED CEMENT PASTES AND MORTARS

H. Hornain[1], J. Marchand[2], V. Duhot[3] and M. Moranville-Regourd[4]

(1) Laboratoire d'étude et de recherche sur les matériaux (LERM)
72-74, avenue Gambetta, 93170 Bagnolet, France

(2) Centre de Recherche Interuniversitaire sur le Béton
Université Laval, Québec, Canada, G1K 7P4

(3) École supérieure de physique et chimie industrielle
10, rue de Vauquelin, 75231, Paris, Cedex 05, France

(4) École normale supérieure de Cachan
61, avenue du Président Wilson, 94235 Cachan, France

(Refereed)
(Received November 29, 1994; in final form September 5, 1995)

ABSTRACT

The diffusion of chloride ions in neat cement pastes and mortars made with and without a limestone filler was investigated. In order to study the effect of the limestone filler, all mixtures were prepared at a fixed water/cement ratio (0,55). Test results indicate that the addition of a limestone filler reduces the diffusion coefficient of chloride ions. This reduction is attributed to the effect of the limestone filler particles on the tortuosity of the system. Results also indicate that the presence of interfaces has only a limited effect on the diffusion coefficient of chloride ions.

Introduction

In recent years, the chloride-induced corrosion of reinforcing bars and the deicer salt scaling deterioration of concrete surfaces have largely contributed to increase maintenance and repair costs of highway networks and marine structures. In order to solve these problems, the diffusion of chloride ions in hydrated cement paste has recently been the subject of numerous studies.

In general, these investigations have emphasized the fact that chloride ion diffusion is an intricate phenomenon depending on numerous interdependent parameters. For instance, the type of coexisting cations and the ambient temperature are known to have a predominant effect on the process [1, 2]. Several reports also indicate that the diffusion of chloride ions is directly influenced by the microstructure of the hydrated cement paste. The diffusion coefficient of chlorides has been found to decrease with a reduction of the water-binder ratio [3, 4] and supplementary cementing materials, such as silica fume, fly ash and slag, are reported to enhance, at various degrees, the resistance of concrete to chloride ion penetration [5- 7].

Despite the fact that limestone fillers are now increasingly used in Europe and North America, very few data are available regarding the effect of these mineral additions on the diffusion of chloride ions in hydrated cement pastes. The only reports on the subject tend to indicate that the use of limestone fillers has no or very little influence on the chloride diffusion coefficient [8, 9].

Research significance

The diffusion of chloride ions in hydrated cement pastes and mortars was investigated. In addition to improve our knowledge of the effect of mineral additions on the transport properties of cementitious materials, this study should also give interesting information on the influence of paste-aggregate interfaces on the diffusion process. In a recent review, Chatterji and Kawamura [10] noted that very little systematic comparisons of the diffusion of chloride ions in hydrated cement pastes and mortars (or concretes) had been published.

Test program

Four different series of mixtures were cast. An ordinary Portland cement was used in a preparation of one mixture of neat cement paste and one mixture of mortar. The same cement, blended with a limestone filler (20% in mass), was also used to prepare another series of paste and mortar mixtures. The water-cement ratio was kept constant (w/c = 0,55) for all mixtures (neat pastes and mortars). In all cases, the limestone filler was considered as an inert material. Doing so is not truly accurate because limestone fillers can partly react with cement and form calcium carboaluminates. However, previous works [11, 12] have shown that to work on a same water-solid ratio basis leads, in the case of the fillerized cement pastes, to an excess of water available for hydration and thus increases the mixture porosity.

The diffusion of chloride ions was studied by means of the diffusion cell method. In addition, the pore size distribution of each set of samples was measured, before and after the diffusion test, by mean of mercury intrusion porosimetry. Scanning electronic microscope (SEM) observations and electron probe microanalysis (EPMA) were also performed to evaluate the microstructure of the specimens and to detect a possible alteration of pore structure resulting from the penetration of chloride ions.

Materials

An ordinary Portland cement (ASTM type I) was used in the preparation of all mixtures. The chemical and mineralogical compositions of the cement are given in Table 1. The second binder was prepared by blending a natural marble (containing 98% of well-crystallized calcite) with the OPC. Blend proportions were fixed at 80% OPC and 20% limestone filler (in mass). The specific area of the limestone filler is of the same order of magnitude as that of the cement. Mortar mixtures were prepared with a natural siliceous sand. Demineralized water was used in the preparation of all mixtures. Mixture compositions are given in Table 2.

Experimental procedures

Cylindrical specimens (diameter = 80 mm, height = 160 mm) of paste and mortar were cast. In order to avoid the bleeding of the neat pastes, a prehydrated slurry of OPC was mixed with the batching water. Such a method has been originally used by Markestad [13] and Mehta [14]. The method is known to substantially reduce bleeding without modifying significantly the water/cement ratio of the mixture. SEM observations of the various mixtures were performed at different magnifications. These observations indicated that if the method of mixing had any influence on the microstructure of the samples, the effects were not visible at any levels of magnification.

TABLE 1 — Chemical and mineralogical compositions

Chemical analysis (%)		Bogue composition (%)	
Silicon dioxide (SiO_2)	21,10	C_3S	58,5
Aluminium oxide (Al_2O_3)	5,07	C_2S	16,3
Ferric oxide (Fe_2O_3)	2,68	C_3A	8,9
Calcium oxide (CaO)	65,42	C_4AF	8,2
Sulfur trioxide (SO_3)	3,37		
Magnesium oxide (MgO)	0,71	Physical properties	
Sodium oxide (Na_2O)	0,09		
Potassium oxide (K_2O)	0,48	Blaine = 3800 cm^2/g	
Titanium dioxide (TiO_2)	0,37	Spec. density= 3.15 g/cm^3	
Manganese oxide (MnO)	0,11		

TABLE 2 — Mixture compositions

Mixture	material	OPC (%)*	filler (%)*	sand (%)*	w/c	w/s
P1	paste	100	0	0	0,55	0,55
P2	paste	80	20	0	0,55	0,44
M1	mortar	25	0	75	0,55	0,55
M2	mortar	20	5	75	0,55	0,44

* Percentage of the total mass of solid materials

Cylinders were kept 48 hours at 20°C and 100% R.H., then demoulded and stored 60 days in a water bath kept at 20°C. At the end of this period, 10-mm thick discs were sawn and immersed for 6 days in a saturated lime solution. Companion samples were also sawn and kept in the same conditions for pore size distribution measurements and microstructural observations.

The discs were then slightly polished and mounted on the diffusion cells (see Fig. 1). A saturated lime solution containing 35 g/L of NaCl was placed in the first compartment of each cell. A saturated lime solution was placed in the second compartment. The diffusion cells were continuously kept at 20°C throughout the entire duration of the test, i.e. for 120 days. The chloride concentration was determined at regular intervals by means of ionic chromatography.

For each mixture, pore size distribution measurements were performed before and after the diffusion test. In order to determine the effect of chloride ions on the pore structure of pastes and mortars, pore size distribution measurements were also carried out on companion specimens kept in a saturated lime solution for the entire duration of the diffusion test (i.e. 120 days). Two specimens were used for each measurement. Samples were dried by cryosublimation before being intruded. In all cases, a contact angle of 141,3° was used in the computations.

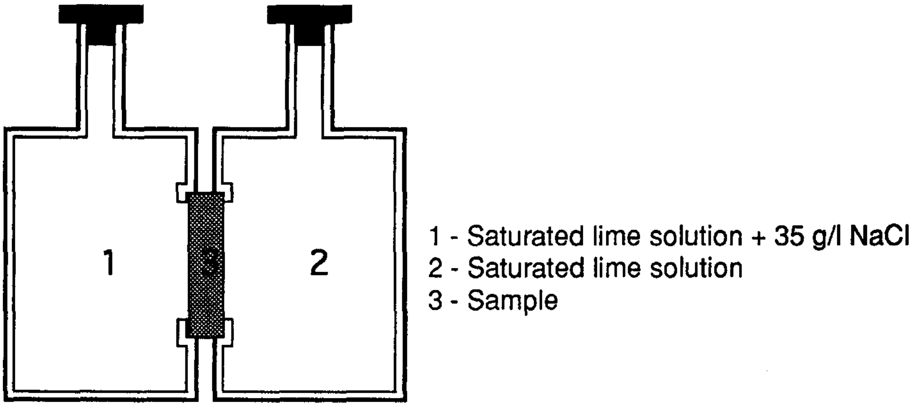

FIG. 1 — Diffusion cell set-up

Test results

Pore size distributions

Test results, before and after diffusion and for the companion specimens, are given in Table 3 and are illustrated by Fig. 2 to 7. In order to take into account the dilution factor associated with the presence of filler grains and aggregates, effective total porosities have been recalculated in mm^3 per gram of cement paste. This calculation rests on the hypothesis that only the hydrated cement paste fraction of each sample was porous and could therefore be intruded by mercury. The recalculated effective total porosities are also given in Table 3.

TABLE 3 - Total porosity measurements

Sample	P1 mm^3/g	P2 mm^3/g	M1 mm^3/g	M2 mm^3/g
Before diffusion a)	134,6	127,9	44,4	44,4
b)	134,6	154,5	155,4	159,2
After diffusion a)	99,9	101,0	42.5	44.1
b)	99,9	122,0	148,8	158,1
Comp. samples a)	110,6	111,3	45,0	47,4
b)	110,6	134,4	157,5	169,3

* a) Measured porosity in mm^3/g of sample. b) Recalculated porosity in mm^3/g of hcp.

Before diffusion, the total porosity of both neat paste mixtures are close to each other, the blended cement paste exhibiting a slightly lower porosity. The total porosity of both mortar mixtures are also very similar. However, when recalculated values are considered, the addition of a limestone filler seems to have affected the pore structure by increasing the total porosity. This appears to be particularly the case for the neat paste mixtures for which the addition of the filler has contributed to increase the total porosity from 134,6 mm^3/g (mixture P1) to 154,5 mm^3/g (mixture P1).

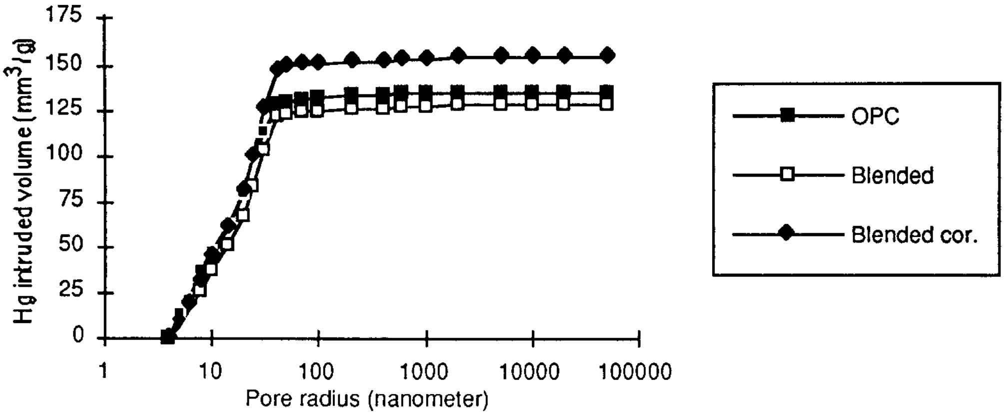

FIG. 2 — Pore size distributions of HCP before diffusion

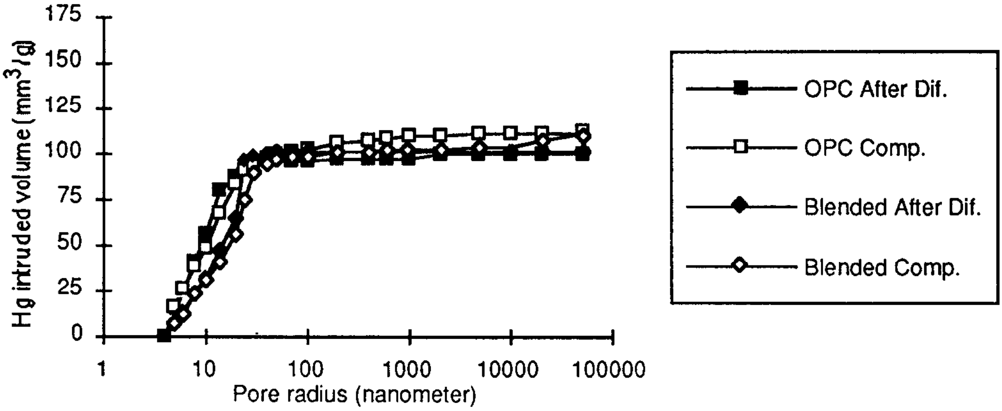

FIG. 3 — Effect of chlorides on the pore size distributions of HCP (uncorrected values)

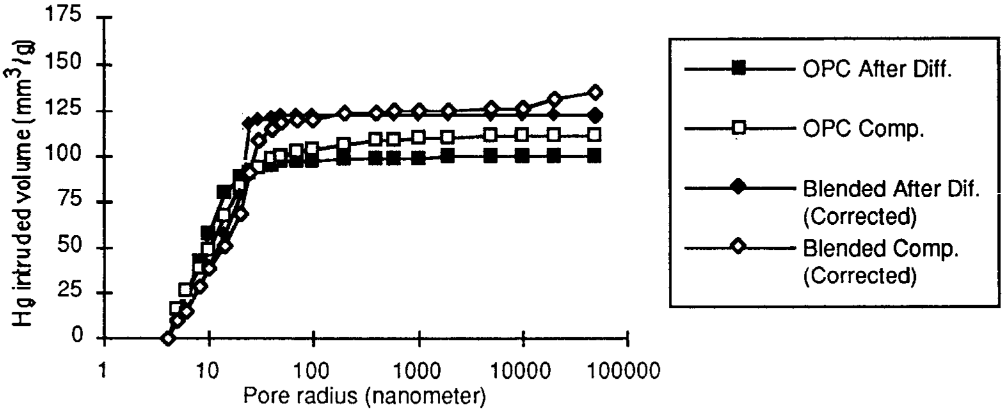

FIG. 4 — Effect of chlorides on the pore size distributions of HCP (corrected values)

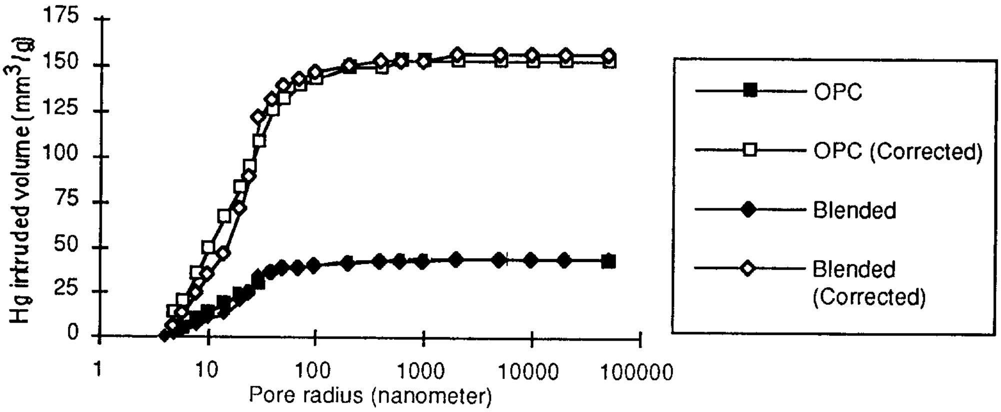

FIG. 5 — Pore size distributions of mortars before diffusion

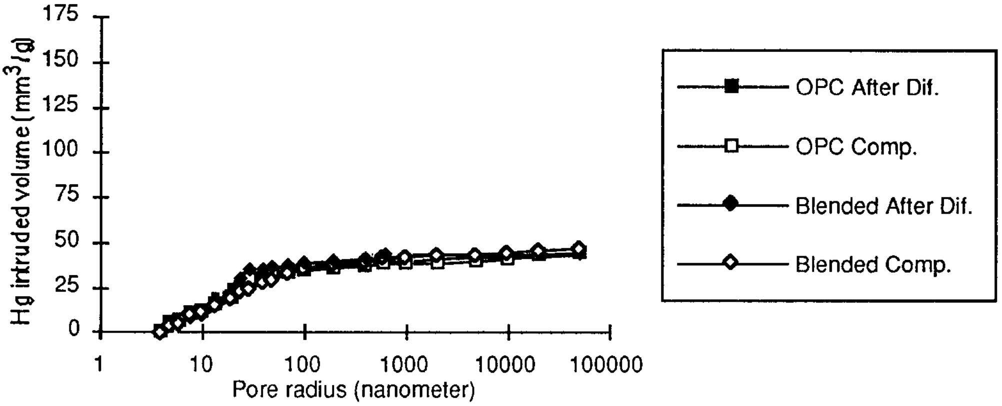

FIG. 6 — Effect of chlorides on the pore size distributions of mortars (uncorrected values)

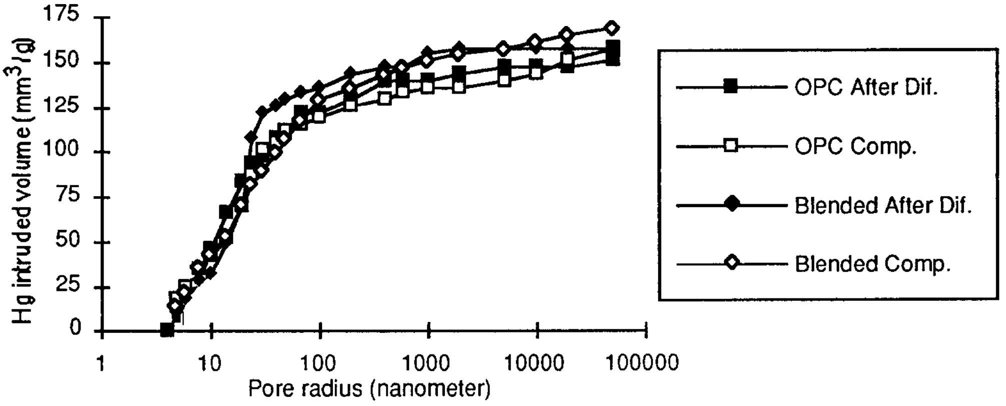

FIG. 7 - Effect of chlorides on the pore size distributions of mortars (corrected values)

The study of the pore size distributions also indicates a marked shift towards the larger pores in the case of fillerized cement pastes. This phenomenon is, however, less apparent for the mortars. As can be seen, the recalculated porosities of mortars are slightly higher than those of corresponding neat paste samples. These results are in accordance with previous published results obtained by making similar assumptions [15]. This increase of the total porosity can be associated with the presence of porous paste-aggregate interfacial transition zones (ITZ) in the mortar samples.

After diffusion, specimens appear to be less porous than companion specimens kept in a saturated lime solution. The presence of chlorides seems to have significantly modified the pore structure of the hydrated cement paste by reducing its total porosity. This effect seems to be particularly important for the neat pastes where the reduction reaches 26% of the initial total porosity for the OPC mixture and 21% for the blended cement mixture (when recalculated values are considered). As suggested by Midgley and Illston [4], this reduction of the total porosity can probably be attributed to the formation of monochloroaluminates and the crystallization of microcrystals of calcium chlorides, and, to a lesser degree, to the accelerating effect of the chloride ions.

As can be seen in Fig. 3 and 4, the chloride ion penetration seems to have also altered the pore size distribution of the neat pastes. For both mixtures, the interaction of chlorides with the hydrated cement paste seems to have resulted in a marked increase of the pores in the of 10 to 50 nm range. Furthermore, paste samples exposed to a chloride solution are characterized by a sharp threshold diameter while companion specimens exhibit a more uniform distribution.

The effect of chlorides appears less evident in the case of mortar samples. As can be seen in Fig. 6 and 7, the pore structure of these specimens does not seem to have been very significantly altered by the presence of chloride ions.

Mineralogy

Before the exposure to the chloride solution, SEM observations confirmed that the microstructure of the cement paste was about the same in all specimens. No clear distinctions could be drawn between specimens made with the OPC and those prepared with the blended cement. In both cases, the cement paste appeared to be dense and well hydrated. As previously mentioned, no clear effect of the neat paste mixing technique could be detected during the SEM observations.

After the penetration of chloride ions, SEM observations revealed some alterations of the hydrated cement paste microstructure. In all cases, the C-S-H appeared to have been attacked by chloride ions and calcium monochloroaluminate crystals had been formed. These crystals seemed to be well integrated to the hydrated cement paste. In pure pastes, containing limestone fillers or not, some of the air bubbles were filled with ($Ca(OH)_2$) crystals. Large calcium hydroxide crystals had also grown on the disc surface in contact with the chloride solution.

EPMA indicated that the silicate hydrates contained chlorides. This tends to confirm the strong interaction between chloride ions and hydrated calcium silicates. However, the nature of the chloride ions in the C-S-H structure was not clear. They could have been substituted, adsorbed or combined in the form of calcium chlorides.

During the SEM observations of all paste and mortar samples, no carboaluminate crystals were observed. The absence of a significant amount of carboaluminates was also confirmed by EPMA.

Diffusion coefficients

Chloride diffusion test results are summarized in Table 4 and illustrated in Fig. 8. Diffusion coefficient (D) and the time (t_0) required to establish the steady-state regime appearing in Table 4 were established by means of linear regression analysis.

Values of D appearing in Table 4 were calculated using the equations derived from Fick's first law by Page et al [3]:

$$J = \frac{V}{A} \cdot \frac{dC_2}{dt} = \frac{D}{e} \cdot (C_1 - C_2) \qquad (1)$$

where:
J = the ionic flux through the disc (moles/cm^2.s^1)
V = the volume of NaCl solution in compartment 1 (cm^3)
A = the area of the disc (cm^2)
e = the thickness of the disc (cm)
D = the effective diffusion coefficient (cm^2/s)
C_1 = the chloride concentration of the solution in compartment 1 (moles/cm^3)
C_2 = the chloride concentration of the solution in compartment 2 (moles/cm^3)

Integration of the above equation gives:

$$\ln\left(1 + \frac{C_2}{C_1 - C_2}\right) = \frac{D \cdot A}{V \cdot e} \cdot (t - t_0) \qquad (2)$$

where: t_0 = the time required to establish the diffusion rate.

If C_1 is and remains always much higher than C_2, equation (2) can be approximated by equation (3) for $t > t_0$:

$$C_2 = \frac{D \cdot A \cdot C_1}{V \cdot e} \cdot (t - t_0) \qquad (3)$$

The value of D can thus be calculated using equation (4):

$$D = \frac{V \cdot e}{A} \cdot \frac{C_2}{C_1} \cdot \frac{1}{(t - t_0)} \qquad (4)$$

The calculation of D using equation (4) implies the following assumptions:

- a quasi-steady diffusion,
- a constant flux through the entire section of diffusion,
- and an unchanging concentration of chlorides at all points of the disc.

In that respect, the coefficients derived from steady-state diffusion experiments should be distinguished from those obtained from unsteady-state experiments [2, 16]. It has been clearly shown that the penetration of chlorides is strongly affected by their chemical and physical interaction with the hydrated cement paste. The chloride ions can be adsorbed on the C-S-H surface and are likely to react with the hydrates or with the remaining anhydrous compounds such as C_3A [4, 17-19]. As previously mentioned, SEM observations and EPMA measurements have clearly indicated that, in the present case, chloride ions did interact with the cement paste hydrates. Since, during an unsteady-state experiment, these interactions are taking place and slowing down the ion penetration, the measured value is often termed the "apparent" diffusion coefficient. During a steady-state experiment, most of the interactions are completed and their effect on the chloride transport are significantly reduced, the measured value can therefore be considered as an "effective" diffusion coefficient.

Since the main objective of this study was to investigate the effect of the limestone filler on chloride transport properties, no corrections for the Nernst and Nernst-Planck retardations of ion mobility were made in the calculations of the diffusion coefficient [20]. Although the value of D calculated according to equation (4) does not represent the "true" chloride ion diffusion coefficient (the value of D will vary with the type and the concentration of the chloride solutions used in the experiment), it can be used on a comparative basis to study the influence of the mixture characteristics on the transport properties.

In order to take into account the dilution factor associated with the presence of mineral inclusions, modified paste diffusion coefficients were also calculated from the measured coefficients. These calculations were made, as suggested by Chatterji and Kawamura [10] and Diab et al. [21], by considering only the portion of the section occupied by the hydrated cement paste (including the interfacial transition zone). The recalculated values of D are included in Table 4 and recalculated chloride diffusion measurements are illustrated in Fig. 9.

TABLE 4 - Effective diffusion coefficients

Mixture	D ($10^{-8}cm^2/s$)	Sa* (%)	Da** ($10^{-8}cm^2/s$)	t_0 ($10^6 s$)
P1	11,25	100	11,25	2,14
P2	5,36	90	5,93	1,98
M1	3,60	43	8,30	1,62
M2	2,42	36	6,63	1,17

* Percentage of the diffusion section occupied by the hydrated cement paste.
** Recalculated diffusion coefficients.

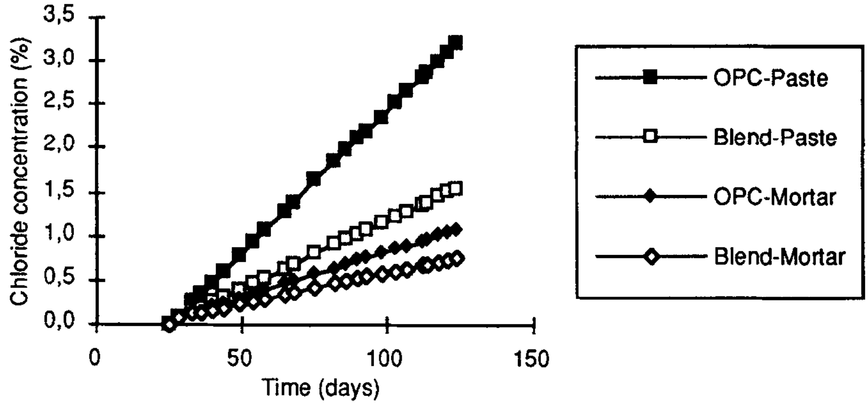

FIG. 8 - Evolution of the chloride concentration in compartment 2

According to the results shown in Table 4, the presence of aggregates does not appear to have the same effect for both series of mixtures. For the two OPC mixtures, the presence of aggregates tend to reduce both the measured and recalculated diffusion coefficients. For blended mixtures, the effect of aggregates is less clear. The measured diffusion coefficient of the blended paste mixture is significantly higher than that of the companion mortar. However, when the comparison is made on the basis of the recalculated values, the opposite trend is observed.

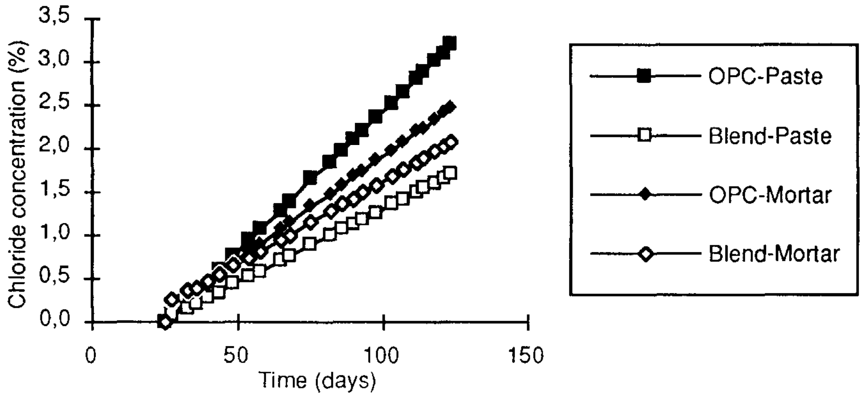

FIG. 9 - Evolution of the chloride concentration in compartment 2 (corrected values)

As can be seen in Table 4, the time t_0 required to establish the diffusion rate varies in the same way as does D. These results tend to indicate that the penetration by chlorides and the subsequent physico-chemical equilibrium in the pores is strongly related to the hydrated cement paste content.

Discussion

The effective diffusion coefficients measured in this investigation are similar to those previously reported in the literature [3, 8, 9]. The values given in Table 4 indicate that the diffusion coefficient appears to be strongly dependent on the hydrated cement paste content (i.e. the presence or not of aggregate particles) and on the limestone filler content.

The reduction of the effective diffusion coefficient associated with the presence of aggregate and limestone filler particles is a little surprising considering the presence numerous ITZ in these mixtures. Several studies have established that the ITZ formed at the vicinity of solid particles is a very thin layer, typically 20-30 µm thick, of hydrated cement paste characterized by a higher porosity and a distinct microstructure [22]. As previously mentioned, the increases in the total porosity of the paste volume fraction of the blended paste and the mortars, as measured by mercury intrusion porosimetry, can be attributed to the presence of these numerous ITZ.

As emphasized by Garboczi et al. [23], the presence of mineral inclusions in a hydrated cement paste matrix has probably two opposite effects on the transport properties. Firstly, the addition of solid (non-porous) particles should increase the tortuosity of the pore structure. Secondly, the presence of porous and connected ITZ may contribute to facilitate the flow of ions or fluids through the sample, the importance of the ITZ connectivity on the transport properties has recently been clearly established by various authors [23-26]. The overall transport properties of a given sample thus depend on the relative importance of these two opposite phenomena and on the ratio of the transport properties of the interfacial transition zone to that of the bulk cement paste.

In the present study, the test results show that the diffusion coefficients of the various mixtures were apparently more influenced by the presence of solid inclusions that increased the pore structure tortuosity than by the presence of (interconnected) ITZ. As previously mentioned, these results are a little surprising particularly if one considers the high solid inclusion (limestone filler + aggregate) content of some of the mixtures studied. In some cases, the volume occupied by the all the solid inclusions was higher than 50% of the total volume of the mixture. According to the models of Winslow et al. [24] and that of Bourdette et al. [25], ITZ in these mixtures should be interconnected or, at least, close to the interconnection level.

The results of the present study are nevertheless in good agreement with the data published by Houst et al. [27] and those reported by Delagrave et al. [28] who also found that the presence of numerous ITZ may, in some cases, have little influence on the diffusion coefficient. These results are also in good agreement with those reported by Skalny and Mindess [29] and Wakeley and Roy [30], who found that permeability was little affected by the ITZ.

Conclusion

The addition of a limestone filler was found to have no detrimental influence on the chloride ion diffusion coefficient of pastes and mortars. At the percentage used in this study, limestone fillers can therefore be added to a mixture without any detrimental influence on its resistance to chloride penetration.

The diffusion of chloride ions was found to be little affected by the presence of numerous ITZ. The little influence of the ITZ on the diffusion coefficient may probably explained by the effect of the limestone filler and aggregate particles on the pore structure tortuosity.

Acknowledgment

The authors thankfully acknowledge the assistance of Mr. Jean-Pierre Commène and Mr. Eddy Zwianziek for their fine technical assistance.

References

[1] FELDMAN, R.F. (1986), 8th Inter. Cong. on the Chemistry of Cement, Rio de Janeiro, Brazil, Vol. 1, Theme 4, pp. 336-356.

[2] ATKINSON, A., NIKERSON, A.K. (1984), J. Mater. Sci., Vol. 19, pp. 3068-3078.

[3] PAGE, C.L., SHORT, N.R., EL TARRAS, A. (1981), Cem. Concr. Res., Vol. 11, pp. 395-406.

[4] MIDGLEY, H.G., ILLSTON, J.M. (1984), Cem. Concr. Res., Vol. 14, pp. 546-558.

[5] KUMAR, A., ROY, D.M. (1986), J. Amer. Ceram. Soc., Vol. 69, N° 4, pp. 356-360.

[6] LI, S., ROY, D.M. (1986), Cem. Concr. Res., Vol. 16, pp. 749-759.

[7] HANSSON, C.M., STRUNGE, H., MARKUSSEN, J.B., FROLUND, T. (1985), Nordic Concrete Research, Vol. 4, pp. 70-80.

[8] RANC, R., MORANVILLE-REGOURD, M., COCHET, G., CHAUDOUARD, G. (1991), ACI Special Publication SP-126, pp. 1239-1257.

[9] COCHET, G., JESUS, B. (1991), Inter. Conf. on Blended Cements in Construction, September 9-12, Sheffield, England, 13 p.

[10] CHATTERJI, S., KAWAMURA, M. (1992), Cem. Concr. Res., Vol. 22, pp. 525-530.

[11] GEGOUT, P., HORNAIN, H., THURET, B., MORTUREUX, B., VOLANT, J., REGOURD, M. (1986), 8th Inter. Cong. on the Chemistry of Cement, Rio de Janeiro, Brazil, Vol. IV, pp. 197-203.

[12] GEGOUT, P., HORNAIN, H., THURET, B., REGOURD, M. (1986), 8th Inter. Cong. on the Chemistry of Cement, Rio de Janeiro, Brazil, Vol. V, pp. 47-52.

[13] MARKESTAD, S.A. (1976), Materials and Structures, Vol. 9, N° 50, pp. 115-117.

[14] MEHTA, P.K. (1975), ACI Mater. J., Vol. 72, N° 10, pp. 573-575.

[15] WINSLOW, D., LIU, D. (1990), Cem. Concr. Res., Vol. 20, pp. 227-235.

[16] MARCHAND, J., GÉRARD, G. (1995), ACI Special Publication SP-154, pp. 169-210.

[17] TANG, L., NILSSON, L.O. (1993), Cem. Concr. Res., Vol. 23, N° 2, pp. 247-253.

[18] BEAUDOIN, J.J., RAMACHANDRAN, V.S., FELDMAN, R.F. (1990), Cem. Concr. Res., Vol. 20, N° 6, pp. 875-883.

[19] HOFFMANN, D. (1984), Cem. Concr. Res., Vol. 14, N° 1, pp. 49-56.

[20] CHATTERJI, S. (1994), Cem. and Concr. Res., Vol. 24, N° 5, pp. 907-912.

[21] DIAB, H., BENTUR, A., HEITNER-WIRGUIN, C., BEN-DOR, L. (1988), Cem. Concr. Res., Vol. 18, pp. 715-722.

[22] OLLIVIER, J.P., MASO, J.C., BOURDETTE, B. (1995), Advn. Cem. Bas. Mat., Vol. 2, N° 1, pp. 30-38.

[23] GARBOCZI, E.J., SCHWARTZ, L.M., BENTZ, D.P. (1995), Advn. Cem. Bas. Mat., Vol. 2, N° 5, pp. 169-181.

[24] WINSLOW, D.N., COHEN, M., BENTZ, D.P., SNYDER, K.A., GARBOCZI, E.J. (1994), Cem. Concr. Res., Vol. 24, N° 1, pp. 25-37.

[25] BOURDETTE, B., RINGOT, E., OLLIVIER, J.P. (1995), Cem. Concr. Res., Vol. 25, N° 4, pp. 741-751.

[26] FAGERLUND, G. (1993), Nordic Seminar on Chloride Penetration in Concrete, January 13-14, Chalmers University of Technology, Göthenburg, Sweden, pp. 321-338.

[27] HOUST, R.F., SADOUKI, F.H., WITTMANN, F.H. (1992), Interfaces in Cementitious Composites, E.F. & Spon, London, pp. 279-288.

[28] DELAGRAVE, A., BIGAS, J.P., OLLIVIER, J.P., MARCHAND, J., PIGEON, M. (1995), Submitted for publication in Advn. Cem. Bas. Mat., 12 p.

[29] SKALNY, J., MINDESS, S. (1984), 10th Inter. Symp. Reactivity of Solids, Dijon, France, pp. 223-224.

[30] WAKELEY, L.D., ROY, D.M. (1982), Cem. Concr. Res., Vol. 12, N° 4, pp. 533-534.