Influence of Microstructure on the Tritiated Water Diffusivity of Mortars

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Four different series of mortars were cast to study the influence of the microstructure on the transport coefficient of tritiated water. Test parameters included type of binder, water/binder ratio (0.25 and 0.45), and sand volume fraction (0% and 50%). Mercury intrusion porosimetry was used to characterize the pore structure of all mixtures. The effective tritiated water diffusion coefficients were determined using a simple diffusion test. The test results show that the reduction of the water/binder ratio and the use of silica fume significantly contribute to reduce the transport properties. The test results also indicate that aggregates modify both the microstructure and the transport properties of mortars. The diffusion coefficient of tritiated water was found to decrease with an increase of the sand volume fraction. The increased tortuosity of the matrix induced by the presence of aggregates thus appears to be more important than the influence of the interfacial transition zone. Results also clearly underline the influence of the preparation technique prior to a mercury intrusion experiment. ADVANCED CEMENT BASED MATERIALS 1998, 7, 60–65. *© 1998 Elsevier Science Ltd.*

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Most concrete durability problems involve the transport of external ions or dissolved chemical species within the material pore structure. Although capillary absorption and permeation can, in certain cases, be of significant importance, most studies tend to indicate that ions are transported mainly through the concrete pore network and microcracks by a diffusion process [1].

Over the years, the complexity of the diffusion process has been emphasized by a large number of experimental studies. The diffusivity of concrete has been found to be influenced directly by a wide range of parameters such as the water/binder ratio, the use of supplementary cementing materials, the binding capacity of hydrated cement paste, and the presence of interfacial transition zones (ITZ) [1–4].

Data on the effect of the ITZ on the transport properties of cement based materials remain, however, limited. Most investigations of the influence of the ITZ on the transport properties have been obtained on model specimens where the complex and random structure of concrete is approximated by simpler geometries. According to some reports, the chloride ion diffusion coefficient of the paste/aggregate interface should be approximately 6 to 12 times greater than that of the bulk cement paste [5–8]. These results are in good agreement with the conclusions of numerous studies where the ITZ was found to have a microstructure significantly different from that of the bulk cement paste. The ITZ microstructure can be roughly characterized by a higher porosity and an increased portlandite content [9–11].

Numerical simulations obtained by Garboczi et al. [12,13] on the electrical conductivity of mortar have indicated that the transport properties of mortars are influenced by the connectivity of ITZ and the increased tortuosity induced by the presence of aggregates. These simulations have also clearly underlined the importance of the ratio of conductivities C_{ITZ}/C_{paste} on the overall transport properties. The significant influence of the pore structure tortuosity has been confirmed recently by several studies where the transport properties of various cement based materials were found to decrease with an increase of the aggregate content [14,15].

As previously stated, most of the investigations that have been actually carried out were conducted on model specimens. The aim of this study is to obtain more information on the influence of the microstructure, particularly that of the ITZ, on the transport properties of mortars. Tritiated water was chosen to study the transport properties of mortars because of the negligible interaction of this molecule with the cement paste hydrates.

Test Program

Four different series of mixtures were cast. Each series was made of a different type of binder. For each series, two mixtures of variable sand volume fractions were prepared. Mercury intrusion porosimetry was used to characterize the pore structure of all mixtures. The

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TABLE 1. Chemical and mineralogical compositions of the cements

Chemical Analysis (%)	ASTM III	ASTM I
Silicon dioxide (SiO_2)	20.48	20.09
Aluminium trioxide (Al_2O_3)	4.03	3.87
Ferric trioxide (Fe_2O_3)	1.78	1.69
Calcium oxide (CaO)	64.73	63.82
Sulfur trioxide (SO_3)	3.33	3.50
Magnesium oxide (MgO)	2.31	2.22
Sodium oxide (Na_2O)	0.36	0.30
Potassium oxide (K_2O)	0.34	0.39
Titanium dioxide (TiO_2)	0.17	0.16
Manganese oxide (MnO)	0.05	0.05
Bogue composition		
C_3S	68.7	68.7
C_2S	6.9	5.8
C_3A	7.7	7.4
C_4AF	5.4	5.1
Physical properties		
Blaine (cm^2/g)	5351	4616

diffusivity of tritiated water was assessed using a simple diffusion test.

Materials and Mixture Characteristics

The water/binder ratio of the first two series of mixtures was fixed at 0.25 whereas the water/binder ratio of the two remaining series was fixed at 0.45. The type of binder used in the preparation of the two high performance series (W/B = 0.25) was an ASTM type III cement. Silica fume (6%, weight basis), used as partial cement replacement, was added to one of these two series. The 0.45 water/binder ratio series were made with an ASTM type I cement. Silica fume (6%, weight basis), used as partial cement replacement, was added to one of these two series. The chemical analyses of the cements are given in Table 1.

For each of the four series, two different mixtures were prepared. The sand volume fractions of each of the two mixtures were 0% and 50%, respectively. A standardized crushed siliceous sand (Ottawa sand C-109) having a specific gravity of 2.60 was used for all mixtures. For the 0.25 water/binder ratio series of mixtures (with and without silica fume), a melamine based superplasticizer was used at a dosage of 2.1% of dry material by mass of binder. The composition of all mixtures is summarized in Table 2.

All specimens for the tritiated water diffusion experiments were cast in plastic molds (diameter = 70 mm, height = 200 mm). The molds were sealed and rotated for the first 24 hours to prevent segregation. At the end of this period, the specimens were demolded and immersed in a saturated lime solution for 3 months. The temperature of the curing bath was kept constant at 23°C.

TABLE 2. Mixture compositions

Mixture	W/B	Cement	Silica Fume (%)	Sand Volume (%)
M25-0	0.25	ASTM III	0	0
M25-50	0.25	ASTM III	0	50
M25(FS)-0	0.25	ASTM III	6	0
M25(FS)-50	0.25	ASTM III	6	50
M45-0	0.45	ASTM I	0	0
M45-50	0.45	ASTM I	0	50
M45(FS)-0	0.45	ASTM I	6	0
M45(FS)-50	0.45	ASTM I	6	50

Experimental Procedures

Mercury Intrusion Porosimetry Measurements

The samples for the mercury intrusion porosimetry were immersed in propan-2-ol for a minimal period of 21 days according to the procedure described by Feldman and Beaudoin [16].

This sample preparation technique was chosen to reduce as much as possible the pore structure alteration induced by drying. At the end of the 21-day immersion period, the samples were vacuum dried at room temperature for 24 hours and tested. All measurements were carried out using a Micromeritics apparatus. The instrument is capable of a minimum intruding pressure of 2.6 kPa and a maximum of 207 MPa. The contact angle assumed for all samples was 130°. For each mixture, a minimum of two samples was tested. To evaluate the influence of the preparation technique on the pore size distribution, two additional samples (M45-0 and M45-50) were prepared in a different way. These samples were not immersed in propan-2-ol but rather were vacuum dried at room temperature immediately after the curing period.

Tritiated Water Diffusion Measurements

The transport properties of the mixtures were assessed using a simple diffusion cell apparatus similar to the one described by Chatterji and Kawamura [17]. The test specimens (5-mm thick, 70-mm in diameter) were first vacuum saturated with deionized water and then mounted on the diffusion cells. The upstream compartment of each cell was filled with a lime saturated solution containing 30.8 MBq/L (10^6 Becquerel/L) of tritiated water. At regular intervals, the concentration of tritiated water in the downstream compartment was measured. As previously explained, tritiated water was chosen to assess the diffusion properties of the mortars because of the negligible chemical interaction of this molecule with the cement paste hydrates [18,19]. Two duplicate specimens were tested for each mixture. The experiments lasted approximately 4 months.

TABLE 3. Porosity measurements

Mixture	Total Porosity (%)	Porosity Paste Fraction (%)
M25-0	8.7	8.7
M25-50	7.5	14.9
M25(FS)-0	4.0	4.0
M25(FS)-50	4.6	9.2
M45-0	22.2	22.2
M45-50	12.2	24.4
M45(FS)-0	18.6	18.6
M45(FS)-50	11.7	23.3

The effective tritiated water diffusion coefficients were obtained from the steady-state regime according to Fick's first law of diffusion:

$$J = -D \frac{\partial C}{\partial x} \tag{1}$$

where J represents the diffusive flux and $\partial C/\partial x$ the concentration gradient.

Test Results

Mercury Intrusion Porosimetry

The mercury intrusion porosimetry test results of the four series of mixtures are summarized in Table 3. As expected, for each of the sand volume contents, the total porosity appears to decrease with the water/binder ratio. As can be seen in Figure 1, the reduction of the water/binder ratio also contributes to the refinement of the pore structure.

The use of silica fume also contributes to the reduction of the total porosity (available to mercury) and the refinement of the pore size distribution (as measured by the pore entry distributions). For example, the total intruded volume is reduced from 22.2% for mixture M45-0 to 18.6% for mixture M45(FS)-0. The reduction of the total porosity when silica fume is added appears to be more important for the high performance mixtures (W/B = 0.25) than for the 0.45 water/binder ratio mixtures. For example, for the neat cement pastes, the total porosity is reduced by almost 54% for the 0.25 water/binder ratio mixtures when silica fume is added whereas this reduction is only 16% for the 0.45 water/binder ratio mixtures.

The presence of silica fume also tends to reduce slightly the threshold diameter. For example, the threshold diameter for the 0.45 water/binder pastes goes from 0.04 μm for the M45-0 mixture to 0.03 μm for mixture M45(FS)-0. The same tendencies can also be observed for the 0.25 mixtures and for every sand volume fraction.

Test results also show that the addition of sand apparently tends to reduce the total intruded volume of mercury. The pore volume data can, however, be recalculated on a unit volume of paste basis considering that only the cement paste is porous. The results of these calculations are included in Table 3. As can be seen, the porosity of the paste fraction of the mortars appears to increase with the sand volume fraction. These results are in good agreement with those reported by Bourdette et al. [5] and Winslow and Liu [20]. They attributed this increase in porosity to the presence of numer-

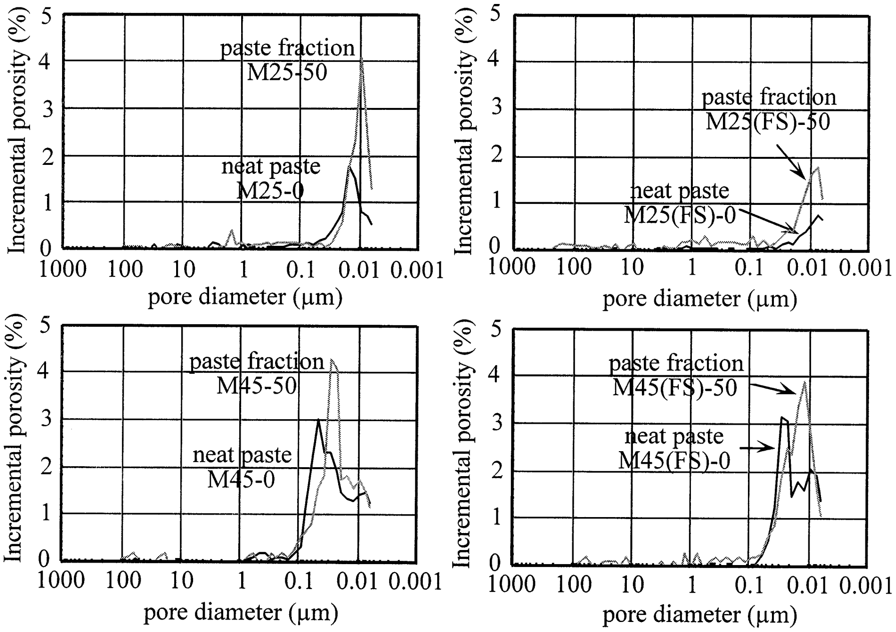

FIGURE 1. Pore size distribution of the paste fraction of mortars.

TABLE 4. Effective tritiated water diffusion coefficients

Mixture	D_{HTO} (10^{-12} m^2/s)
M25-0	0.63
M25-50	0.38
M25(FS)-0	0.16
M25(FS)-50	0.11
M45-0	9.83
M45-50	4.58
M45(FS)-0	3.79
M45(FS)-50	0.79

ous porous ITZ in the materials. This increase in porosity appears to be more important for the 0.25 water/binder ratio mixtures than for the 0.45 water/binder ratio mixtures. For example, the increase in porosity of the paste fraction, compared to the porosity of the neat paste samples, is 71% for the M25 mixtures whereas it is only 10% for the M45 mixtures.

Figure 1 presents the pore size distributions of the neat cement pastes and that of the paste in the corresponding mortars with 50% sand. The presence of aggregates tends to increase the volume of small pores, and the overall distributions are slightly shifted toward the finer pores.

Tritiated Water Diffusion Coefficient

The effective tritiated water (HTO) diffusion coefficients are summarized in Table 4 and Figure 2. These results clearly emphasize the predominant influence of the water/binder ratio on the diffusion process. As can be seen, a reduction of the water/binder ratio from 0.45 to 0.25 leads to a significant decrease of the diffusion coefficient of tritiated water by almost an order of magnitude. The use of silica fume also contributes to reduce the diffusion coefficient. The effective diffusion coefficient of tritiated water is at least 2.5 times lower when silica fume is used.

The results also indicate that the addition of sand contributes to reduce the diffusion of tritiated water. The diffusion coefficients are at least 2 times lower when 50% of sand (volume fraction) is added to the neat cement paste.

Discussion

The test results of the present study clearly indicate that the reduction of the water/binder ratio and the use of silica fume are two excellent ways of reducing the diffusivity of cement based materials. These observations are in good agreement with those of other authors [21,22].

The results of the tritiated water diffusion experiments are particularly interesting to analyze considering the little chemical interaction of this molecule with the cement paste hydration products. The transport of tritiated water should therefore be predominantly affected by the material pore structure characteristics (such as tortuosity and constrictivity). According to the tritiated water diffusion data, a reduction of the material total porosity (as shown by the mercury porosimetry measurements even though mercury porosimetry measurements do not represent the "true" porosity) clearly contributes to significantly influence the diffusion coefficient. However, there seems to be no straightforward relationship between the two parameters. For example, the total porosities of the M45 and M45(FS) series of mixtures are quite similar whereas the tritiated water diffusion coefficients of the M45(FS) mixtures are several times lower than those of the M45 mixtures. Obviously, the material pore structure characteristics plays an essential role in the diffusion process.

As previously described, according to the mercury intrusion porosimetry test results, silica fume appears to be more efficient in reducing the total porosity for the high performance mixtures than in the 0.45 water/binder ratio mixtures. The porosity measured by a mercury intrusion experiment is only the porosity that is available to mercury, which is governed by the pore entries and the continuity of the pore network. The addition of silica fume to high performance mixtures probably creates pores with very thin entries that are not accessible to mercury whereas for the 0.45 mixtures, the refinement of the pore structure creates pores with entries that are still accessible to mercury.

In the present investigation, the porosity of the paste

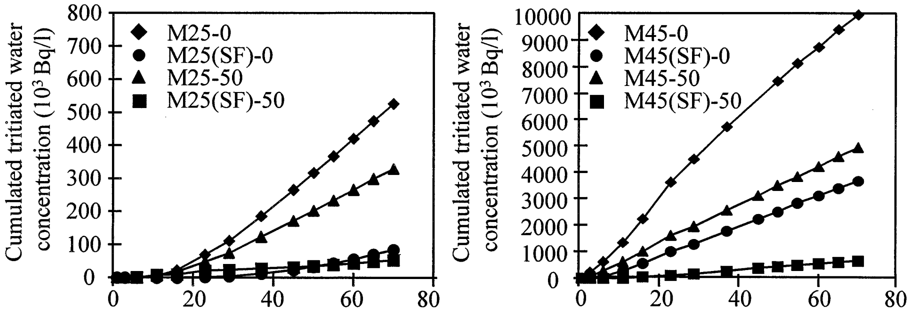

FIGURE 2. Evolution of the concentration in the downstream compartment.

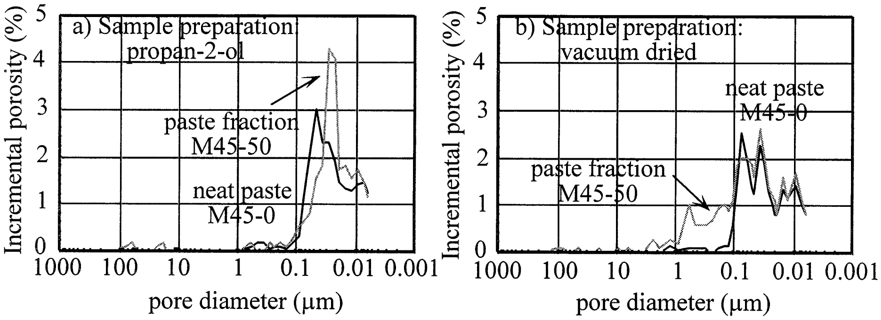

FIGURE 3. Influence of the sample preparation technique on the pore size distribution.

volume fraction of the mortars was found to increase with the sand volume fraction. This increase in the porosity can be attributed to the presence of numerous ITZ in the materials. As previously mentioned, the ITZ tends to be more porous than the bulk cement paste. Since there is water conservation in the mortar, a higher water/binder ratio in the ITZ will result in a lower water/binder ratio in the bulk cement paste. The microstructure of the neat paste is thus not totally similar to the bulk paste of the mortar.

The change in the pore size distribution, resulting from the addition of aggregates to the neat cement paste, appears to be particularly important for the 0.25 water/binder ratio mixtures. At a water/binder ratio of 0.45, this phenomenon probably has little influence, since most of the pore volume of neat pastes is available to mercury. At 0.25, however, the fraction of the total pore volume available to mercury is probably relatively low in neat pastes but higher in mortars because of the change in the pore size distribution due to the ITZ.

The increased pore volume associated with the presence of ITZ was detected mainly in the small pore region (i.e., for pores with diameters ranging from 0.01 to 0.1 μm). At first glance, these results appear to be in contradiction with several sources in the literature [5,23,24]. For example, it has been shown by several authors that the addition of sand generally leads to an increase in the volume of pores with diameters between 0.1 and 1 μm. These authors attributed this opening in porosity to the presence of numerous ITZs. The difference in the pore size distributions between those obtained by these authors and those presented in this paper can probably be explained, at least in part, by the sample preparation technique prior to intrusion.

Figure 3 presents the influence of the sample preparation technique on the pore size distribution for the neat cement paste (M45-0) and the paste fraction of the mortar with a sand volume fraction of 50% (M45-50). The distributions in Figure 3a were obtained on samples that were immersed in propan-2-ol prior to intrusion according to the procedure developed by Feldman and Beaudoin [16]. The distributions in Figure 3b were obtained on samples of the same mixtures that were immediately vacuum dried after the curing period. As can be seen in the figure, the pore size distributions greatly depend on the sample preparation technique before the mercury intrusion. The opening of the 0.1- to 1-μm pore volume associated with the addition of sand is clearly visible in Figure 3b, which corresponds to the samples that were vacuum dried prior to intrusion. This tends to indicate that the ITZs are somewhat more fragile than the bulk cement paste. Severe drying treatments may contribute to favor the formation and the interconnection of microcracks in the ITZ that artificially modify the initial pore structure of the material. The influence of the preparation technique on the mercury intrusion porosimetry test results observed in this series of tests is in good agreement with the results published by Konecny and Naqvi [25].

The increase in porosity of the paste fraction of mortar compared to that of the neat paste samples can also probably be explained by the degree of hydration of the mixtures. As shown by Breton [26] and Bourdette et al. [5], the porosity of the ITZ decreases very rapidly in the first 3 months of curing. Even if the porosity of the ITZ is still coarser than that of the bulk cement paste, mercury has to penetrate through the bulk paste before reaching the ITZ. This could explain why the increase in porosity was detected mainly in the small pore region. It is also possible that this increase in porosity of the paste fraction of mortars could also be attributed, at least in part, to the air void content of the mortars, even though many precautions were taken to avoid air entrainment. Diamond and Leeman [27] clearly show that the increase in porosity due to air entrainment, as measured by mercury intrusion porosimetry, was detected mainly in the finer pore regions.

The evolution of the effective diffusion coefficients as a function of the sand volume fraction can be seen in Table 4. The results of the effective diffusion coefficients of tritiated water clearly show a decrease of the transport properties of mortars with the increase of the sand volume fraction. These results are in good agreement with conclusions of previous studies [12–15].

The presence of aggregates in a hydrated cement paste matrix probably has two opposite effects on the transport properties. First, the addition of solid particles leads to an increase in the tortuosity of the matrix while reducing the total space available to diffusion. This implies that the diffusing particle has to move around the solid inclusions. Second, the presence of porous ITZ probably contributes to facilitate the movement of ions, particularly if they are interconnected, and, in addition, implies that the bulk paste is very dense, which can also slow down the movements of diffusing species. The overall transport properties of a given mortar sample are thus a function of the relative importance of these opposite phenomena [12,13]. The test results of the present study tend to show that the overall transport properties of the mortars were more influenced by the increased tortuosity associated with the presence of the aggregates than by the presence of connected ITZ, especially for the M45(FS)-50 mixture. These observations are particularly interesting considering that numerical simulations have demonstrated that more than 90% of the ITZ in the mortars with a sand volume of 50% was found to be interconnected [14].

It should also be emphasized that the influence of the aggregates on the transport properties is not the same for all mixtures (Table 4). For the mixtures containing no silica fume, irrespective of the water/binder ratio, the aggregates reduce the diffusion coefficient by approximately 50%. For the mixtures containing silica fume, however, there is a large decrease for the 0.45 water/binder ratio mixture (80%) but much smaller for the 0.25 water/binder ratio mixture (30%). It can be hypothesized that the reduction of the diffusion coefficient is related to the pore structure of the material. The addition of silica fume to the 0.45 water/binder ratio mixture contributes much more to the refinement of the pore structure than in the 0.25 water/binder ratio mixture.

Conclusion

The test results presented in this article clearly indicate that the reduction of the water/binder ratio and the use of silica fume, by modifying the microstructure of the hydrated cement paste, contribute to slow down the diffusion of tritiated water.

The presence of aggregates in a neat cement paste was found to modify the microstructure and the transport properties of cementitious systems. The results presented show a global reduction of the transport properties of mortars with the increase of the sand volume fraction. They also indicate that the modifications due to the presence of aggregates varies with the matrix composition, which influences the porosity of the ITZ.

The mercury intrusion porosimetry test results also clearly underline the importance of the sample preparation technique prior to intrusion.

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