Influence of microstructure on tritiated water diffusivity in mortars

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ABSTRACT. The present study aims to investigate the influence of mortar’s microstructure, particularly the effect of aggregates content and the aggregate-paste ‘interfacial transition zone’ (ITZ), on tritiated water diffusivity of cement-based materials. To this end, three different series of mortars were prepared and tritiated water diffusion tests are conducted. Variables are water-to-cement ratio, sand volume fractions and particle size distribution. In parallel, microstructure of these materials is characterized by water porosimetry, mercury porosimetry and by backscattered electron microscopy associated to images analysis. It was observed that at low sand content (0% - 50%), diffusion properties of mortars are dominated by aggregates dilution effect. At 60% sand, diffusion increases significantly suggesting that a pores percolation threshold has been reached. Tests results indicate also that sand particle size distribution has a great impact on the diffusivity of mortars.

RÉSUMÉ. La présente étude consiste à étudier l’influence de la microstructure des mortiers sur la diffusion de l’eau de tritiée au sein de ces matériaux, en particulier, la concurrence entre l’effet diffusive des ITZs et l’effet des granulats non diffusif. À cette fin, plusieurs séries de tests de diffusion de l’eau tritiée sont menées sur des mortiers ayant différents rapport eau sur ciment, différentes fractions volumique de sable et différentes granulométries. En parallèle, la microstructure est caractérisée par porosimétrie au mercure, porosimétrie à l’eau et par l’analyse d’images MEB. Il a été observé que, à faible teneur en sable (0% - 50%), les propriétés de diffusion des mortiers sont dominées par l’effet de dilution des granulats. À 60% de sable, la diffusion augmente considérablement suggérant qu’un seuil de percolation de pores est atteint. Les résultats des essais indiquent également que la granularité du sable a un impact important sur la diffusivité des mortiers.

KEY WORDS: Tritiated water diffusion; Mortar; Concrete; Microstructure; Interfacial Transition Zone; percolation.

MOTS-CLÉS : Diffusion d’eau tritiée ; mortier ; béton ; microstructure ; auréole de transition ; percolation.
1. Introduction

Concrete durability continues to be a subject of considerable interest, especially with the use of cement based materials in nuclear industry for the containment of low and intermediate level radioactive waste. One key parameter of the durability of concrete is the diffusivity, according to most studies [RIC 92, BEJ 06, BAR 06, BEJ 07a, BEJ 07b, and STO 07]. In the literature, a lack of available experimental data subsists about the tritiated water diffusivity of mortars and concretes. In fact, it was suggested that tritiated water (HTO), the liquid form of tritium, has negligible interaction with cement paste hydrates [RIC 92] which allows the measurement of effective transport parameters of the material. Besides, the diffusion of HTO is purely molecular and Fick’s law can then be applied.

This study aims to carry out an experimental investigation to enhance the understanding of link between microstructure and tritiated water diffusivity of saturated mortars. The effect of aggregates presence via the ITZ (Interfacial Transition Zone) on transport properties and materials durability is also studied. In fact, even if the effect of such aggregate-paste interfaces on mechanical properties is demonstrated and is of considerable significance [SCR 04], their impact on transport properties remains ambiguous.

Several series of tritiated water diffusion tests were conducted on mortars characterized by different water-to-cement ratios, sand volume fractions and particle size distribution. In parallel, microstructure of these materials is explored by mercury and water porosimetry, SEM images and images analysis.

2. Materials and Methods

Three different series of mixtures were prepared. In series S1, mortars were used with water to cement ratio (w/c) varying between 0.3 to 0.5 with the same sand content (50%). In series S2, five different sand volume fractions were tested (0%, 10%, 30%, 50% and 60%) at 0.4 water to cement ratio. S1 and S2 mortars were cast with standardized sand (SN). Series 3 (S3) consisted of three formulations of different grain size (mm): fine sand (0.125/0.3) labeled SF, standardized (EN 196-9) sand (0.08/2) labeled SN and a coarse siliceous sand (0.63/2) labeled SG. S3 mortars were prepared at w/c = 0.4 and with 50% of sand.

Natural siliceous sand (98.5% silica) with density of 2.63 and 24h-absorption of 0.4% is used in all formulations.

Mortars were prepared by mixing Portland cement (European grade CEM I 52.5N CE PM-ES-CP2 NF) with the required quantity of tap water in a mechanical mixer. Mixtures preparation was based on the standard of normalized mortar fabrication procedure NF EN 196 - 1. A modified polycarboxylic ether polymers-based superplasticising admixture (Glenium® 27) was used at low water/cement ratio (w/c = 0.3 and w/c = 0.35) and at high amount of sand grains (S2.60% and S3.SF) in order to improve workability. Mixture proportions are given in Table 1.
Table 1. Mixture proportions of mortars samples. SN for normalized sand (0.08/2), SF for fine sand (0.125/0.3), SG for coarse Sand (0.63/2).

<table>
<thead>
<tr>
<th>Series</th>
<th>Mixture ID</th>
<th>Water/Cement ratio</th>
<th>Sand volume fraction</th>
<th>Particle size</th>
<th>Glenium®27 (% wt. Cement)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>S1.0,3</td>
<td>0.3</td>
<td>50%</td>
<td>SN</td>
<td>0.50%</td>
</tr>
<tr>
<td>S1</td>
<td>S1.0,35</td>
<td>0.35</td>
<td>50%</td>
<td>SN</td>
<td>0.50%</td>
</tr>
<tr>
<td>S1</td>
<td>S1.0,4</td>
<td>0.4</td>
<td>50%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S1</td>
<td>S1.0,5</td>
<td>0.5</td>
<td>50%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>S2.0%</td>
<td>0.4</td>
<td>0</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>S2.10%</td>
<td>0.4</td>
<td>10%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>S2.30%</td>
<td>0.4</td>
<td>30%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>S2.50%</td>
<td>0.4</td>
<td>50%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>S2.60%</td>
<td>0.4</td>
<td>60%</td>
<td>SN</td>
<td>0.50%</td>
</tr>
<tr>
<td>S3</td>
<td>S3.SF</td>
<td>0.4</td>
<td>50%</td>
<td>SF</td>
<td>0.50%</td>
</tr>
<tr>
<td>S3</td>
<td>S3.SN</td>
<td>0.4</td>
<td>50%</td>
<td>SN</td>
<td>-</td>
</tr>
<tr>
<td>S3</td>
<td>S3.SG</td>
<td>0.4</td>
<td>50%</td>
<td>SG</td>
<td>-</td>
</tr>
</tbody>
</table>

2.1. Samples preparation and conservation

Cylindrical samples (7Ø×11 cm) were cast. The molds with fresh mortars are closed with plugs to avoid evaporation for the first 24 hours. Then, samples are demolded and immersed in a saturated lime solution for 3-month period at 20±1°C. After the curing period, the samples are sectioned from the center to produce two 6 mm thick discs to be used for transport testing.

2.2. Porosity measurements

2.2.1. Water porosity measurements

The samples were dried in an oven at the temperature of 60°C until constant weight was reached. Duplicate samples were tested for each formulation and the mean is reported as result.

2.2.2. Mercury intrusion porosimetry

Centimetre-scale samples were first frozen (-196°C) by immersion in liquid nitrogen. After freezing, samples were introduced for 7 days in a freeze-dryer in
which vacuum were kept to $10^{-3}$ Pa. Freeze drying was proved to be the least damaging drying technique [Gal 01].

Tests were carried out using a Micromeritics porosimeter with a maximum 413 MPa injection pressure. The contact angle was 130° for all samples. The minimum pore access diameter reached is about 3 nm. For each formulation, two samples were tested.

### 2.3. Backscattered electron microscopy

A scanning electron microscope in the backscattered electron mode (BSE) associated with images analysis was used to investigate spatial distribution of detectable porosity at paste / aggregate interface (ITZ).

Electronic microscopy was conducted on samples conserved according to procedure described in §2.1. Before vacuum impregnation, samples are freeze dried for 7 days and finally diamond polished in successive stage to a 0.3 µm surface finish. The microscope was operated at high vacuum ($3.68 \times 10^{-4}$ Pa), 20 kV accelerating voltage and 15 mm free working distance. Images analysis procedure was based on Euclidean distance mapping approach [WON 06]. This method permits the determination of phase distribution plots quickly and efficiently.

### 2.4. Diffusion measurements

The basic arrangement used to measure the steady state diffusion coefficient was similar to that employed by Richet [RIC 92] and Nugue et al. [NUG 07]. It consists on putting the mortar sample between two compartments. The samples were sealed into position using an “Araldite®” epoxy adhesive and by means of O-rings to avoid leakage. Each compartment of 111±1 ml volume is filled with an alkaline solution (NaOH= 0.1 mol/L; KOH=0.1 mol/L; CaO= 2 mmol/L) in order to prevent the leaching of the alkaline cement pore solution. Then the cells were left to stand for about fifteen days so that the mortars pore solution is in equilibrium with the alkaline solution introduced in both upstream and downstream compartment. After this period, tritiated water was incorporated in the upstream compartments at equal concentration. The experiment consisted then of measuring the concentration of tritiated water in the downstream compartment as function of time $t$.

The upstream concentration $C_0$ and downstream one $C_1$ were maintained constant for all $t$ ($C_0 = 3.2 \times 10^6$ Bq/L; $C_1=0$) and the initial concentration in the sample was set to zero. In order to fulfil boundary conditions, the downstream compartment is drained and filled with a fresh alkaline solution as soon as the downstream activity has reached 3% of the upstream one. In all diffusion experiments, the temperature was controlled at 20 ±1°C.

Since the diffusion of tritium is purely molecular, Fick's laws can be applied. The effective tritiated water diffusion coefficients were obtained from the steady state regime according to Fick’s first law of diffusion.
3. Results and discussion

3.1. Water porosity

Average relative error is about 1%. As expected, porosity values increased with the water to cement ratio (w/c) (Fig. 2a).

Fig. 2b shows results of water porosities evolution with increasing aggregate content of mortar. These are compared to \((1-V_{ag})\) linear plot representing theoretical case of porous medium diluted by non porous aggregates. It can be seen that experimental results and \((1-V_{ag})\) plot are close. This confirms that presence of aggregates does not disturb the overall paste matrix porosity, which is expected since these formulations have the same water to cement ratio \((w/c = 0.4)\).

At equal sand volume fraction and equal water to cement ratio, formulations with different aggregates size distributions have almost the same porosity value (Figure 2c). In general, water porosimetry results prove that the main parameter controlling water porosity value is the water to cement ratio. In another hand, oven drying technique may be not sensitive enough to detect small changes on samples pores distribution. In fact, as will be shown later, for same water porosity (S3 samples), HTO diffusion coefficient can be greater by more than three times.

![Figure 1. Effect of water to cement ratio (a) aggregate content (b) and sand particle size distribution (c) on mortars water porosities](image-url)
3.2. Mercury Porosity

The aggregates used to prepare mortar samples were non-porous, so that the measured pore volume concerns solely the bulk (paste fraction). For this reason, in the results shown herein, the pores volumes of all samples were expressed on a mass of paste rather than the mass of mortar. Figure 2 shows cumulative intrusion curves for a series of mortars of increasing sand content (Figure 2a), increasing water to cement ratio (Figure 2b) and finally of different aggregate size distributions (Figure 2c). In general, test results show that the presence of aggregates modifies the pore structure of mortars which is in agreement with other studies [WIN 94, BOU 95, and CAR 03]. In fact, mortars contain large pore size (0.1 – 1 µm) which is not observed in cement paste and may be attributed to ITZ pores.

For aggregate fraction of less than 50%, the addition of sand tends to reduce the total intruded volume of mercury (Figure 2a). As the sand content increase from 50% to 60% there is a sudden increase of intruded pore volume at about 0.6 µm suggesting the interconnection of this family of pores.

At the same sand content (50%), the mercury intrusion results (Figure 2b) show the increasing of both capillary pores (0.01 µm – 1 µm) and C-S-H pores (≤ 0.01 µm) with water to cement ratio. The amount of ITZ pores increases with w/c ratio but remains accessible only via bulk paste, that’s why no percolation was observed at 50% sand mortars. This may confirms that percolation threshold is above 50% for aggregates size distribution used in this study (Standardized Sand).

Between fine and coarse particle sizes (Figure 2c), there is great difference in cumulative intrusion curve. Mercury total porosity for the fine sand (SF) mixture is higher than that of the coarse (SG) and normalised (SN) sand, in spite of quite similar total water porosities of the three mixtures (Figure 1).

Moreover, volume fractions of ITZ were calculated for each formulation from aggregates size distribution assuming spherical particles. The approach used was developed by Lu and Torquato [LU 92] and applied by Garboczi and Bentz [GAR 98] to mortars and concretes. According to these calculations, the corresponding ITZ volume fraction of S3.SG mixture is 5.75% that for S3.SF mixture is 25.5% (about four times higher). This can be also the cause of the large difference in the mercury intrusion results (Figure 2c). Same calculations of ITZ volume fractions were run for S2 mortars and showed the same trend as MIP results.
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Figure 2. Effect of aggregate volume fraction (a), water to cement ratio (b) and particle size (c) on pores connectivity.

3.3. ITZ porosity from SEM images analysis

Figure 3 shows an example of typical BSE image captured at high magnification of S2.50% mortar. Using image analysis, the distribution of detectable porosity in the aggregate/paste interface for S2.50% mortar is determined (Figure 4).

Figure 3. Typical BSE image of Portland cement mortar (1 year old, w/c =0.4)

A reduction in porosity with distance from aggregate surface is evident and in line with previous findings [MON 85, SCR 88, SCR 96]. The detectable porosity decreased from 25% at the boundary to 10% at 20 µm from the aggregate. More studies will be carried to investigate the effect of aggregate size and sand volume fraction on the porosity gradient at the ITZ. But in general results proves that the existence of such interface is no longer a doubt.
3.5 Effective Diffusion Coefficient

Effective diffusion coefficients plotted against water to cement ratio, aggregate volume fraction and aggregate size distribution are shown in Figure 5. Each data point is an average of two replicates and the errors bars indicates +/- standard deviation. The variability between replicates is relatively small compared to between different formulations so that averaging permit meaningful comparison.

Experimental results prove that diffusion coefficient increases with water to cement ratio (Figure 5a). At low sand content (0 - 50%), the diffusivities of the 0.4 w/c ratio mortars decreased with sand content by a factor of 1.5 to 2, but increased significantly at 60% (Figure 5b). This result has been confirmed with MIP results. It can be assumed that percolation of ITZ pores occurred at 60%. There are similar results in some previous studies [HOU 92, BOU 94].

The effect of particle size distribution is described in (Figure 5c). The result shows an important influence of aggregate particle size on diffusion process. S3.SF (fine sand) diffusivity is three time higher than S3.SG (coarse sand) one. It was also observed that variation of effective diffusivity is well correlated with the estimated volume fractions of ITZ in each formulation. For this reason, the higher diffusivity of the SF (fine sand) mortar can be attributed to a greater volume fraction of ITZ in this material (25 %) leading to the formation of percolated cluster of ITZ phase.
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Figure 5. Effect of water to cement ratio (a), aggregate volume fraction (b) and aggregate particle size (c) on mortars diffusivity

4. Conclusion

This study aims at improving the understanding of the transport properties of mortars according to their formulations. The main intention is to obtain a better estimate of the effective diffusivity in the liquid phase by considering the link between microstructure and transport properties in mortars.

The results show that adding aggregates can lead to an increase of the value of the diffusion coefficient if the amount of sand and his own particle size distribution allow the formation of a percolating cluster. Existence of porous zone close to aggregate is no longer a doubt; it’s a region of gradually changing microstructure. However, others studies are needed to reveal the effect of aggregate size and sand content on such interface.

Coupled with sand content, the sand particle size distribution has a great impact on the diffusivity of mortars. At the same sand volume fraction, the use of coarser aggregates leads to less diffusing material.

Finally, the increase in the water to cement ratio at constant volume of sand increases diffusion process by formation of large capillary pores. However, it seems that at same sand content, increasing water to cement ratio does not promote ITZ percolation.
5. References


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