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The validity of the formation factor concept from through-out diffusion tests on Portland cement mortars

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ABSTRACT

The diffusion coefficients of ions and radionuclides in cementitious materials are the basic parameters to evaluate the state of the degradation of structures. In this article, three different tracers (two ions, and a radionuclide) were tested on the same formulations of mortars (sand volume fractions from 0 to 60%) in terms of the through-out diffusion, to determine the effective diffusion coefficients of each tracer and each formulation. The aim of this study is to prove the validity of the formation factor equation relating the effective diffusivity of a tracer in cementitious material to its diffusion coefficient in pure water. This result is extremely interesting because once the geometric formation factor of a material is known, it is possible to determine the values of the effective diffusion coefficients of any other diffusing species in this material.

1. Introduction

The study of the long-term behavior of cementitious materials remains a topic that arouses the interest of many scientists because these materials are used in diverse structures. In particular, cement-based materials are largely used in the nuclear industry for the construction of nuclear power plants and infrastructure dedicated to radioactive waste storage and disposal.

In such projects of durable constructions, diffusive transport in the interstitial solution - contained in the porosity of concrete-is one of the most important factors that determines the lifetime of concrete structures.

In civil engineering, chloride diffusion continues to be the subject of several studies, regarding its influence on the corrosion of steel bars used as reinforcement in concrete structures. Thus, the diffusion coefficient of chloride is one of the key parameters in the prediction of the degradation level of cementitious materials.

After developing experimental tests based on diffusion such as migration tests [1–6], or immersion tests [7,8], the interest of researchers turned to the study of the influence of aggregate in mortars and concrete on chloride ingress and the effect of the interfacial transition zone (ITZ) [9,10] and modeling of transport properties in cement based materials [11,12].

In the framework of nuclear waste storage and disposal, the liquid form of tritium (HTO) is considered to be an ideal tracer for the characterization of the effective diffusivity in cementitious materials, because of its negligible interaction with the cement matrix [13,14]. However, the radioactive nature of HTO encourages the determination of nonradioactive elements (generally ions) that can provide an effective diffusion coefficient without having to perform tritiated water diffusion tests.

Among different possibilities, through-out diffusion tests [15,16] were adopted in this study. The transport mechanism in this test is very similar to the one that takes place in real structures.

Only diffusion in saturated porous materials is examined in this study. Electro-diffusion and the unsaturated conditions are ignored hereafter. Thus, the aim of this research is to validate the formation factor equation (Eq. (1)) which makes it possible to deduce the effective diffusion coefficients of any other species that reacts weakly with the cement matrix, by only knowing the formation factor of the tested material.

$$F = \frac{D_0^{HTO}}{D_e^{HTO}} = \frac{D_0^{ion}}{D_e^{ion}} \tag{1}$$

Where F is the formation factor of the cementitious material; (D_e^{ion}, D_e^{rad}) are the effective diffusivity of ions and radionuclides

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respectively in the cementitious material; and (D_0^i) is the diffusion coefficient of the specie "i" in an infinitely diluted solution (usually in pure water) at 25 °C.

For that purpose, several formulations of mortars were tested in regard to through-out diffusion with HTO and ions (lithium and chloride) which allowed for the identification of their diffusion coefficients.

Diffusion of lithium and chloride was performed at low concentrations of 41 mmol/L in order to neglect the effect of the electrical interaction between diffusion species and an ionic pore solution, and to use the linear reversible binding hypothesis.

2. Experimental procedures

2.1. Test program

To achieve previously stated goals, seven different mixtures were prepared. Mortars were manufactured by mixing Portland cement (European grade CEM I 52. 5 N CE PM-ESCP2 NF) with standardized siliceous sand CEN IN 196-1 labeled SN (the granulometric distribution of SN is shown in Table 1) and with water and super plasticizer (Glenium 27) for some formulations. These formulations were made by fixing the water-to-cement ratio (w/c) and by varying the relative aggregate volume content (C_{ag}) to generate different geometrical formation factors for each specimen. Table 2 provides the compositions of the tested materials.

Mortar specimens were mixed according to the standard mortar fabrication procedure NF EN 196-1 and were cast in PVC cylinders (70 mm diameter and 110 mm height). After 24 h, the specimens were demoulded and conserved in lime water. They were cured in a humid chamber at T = 20 ± 1 °C for a period exceeding three months to ensure complete hydration of the material and to produce a "fixed" microstructure during all of the experiments. The samples used for diffusion tests are 6 mm thick discs obtained by the underwater cutting of the central portion of each specimen.

2.2. Microstructure analysis

The microstructure of the studied materials was investigated by free water porosity and by Mercury Intrusion Porosimetry (MIP) measurements.

2.2.1. Free water porosity measurements

Water porosity is considered as a key parameter in the durability assessment of cementitious materials [17]. The experimental method following the AFPC-AFREM protocol [18] consists of determining the water porosity by weighing under the following three scenarios: the sample water saturated mass M_s, the sample dried mass M_d, and the sample mass when immersed in water M_w.

The dried mass was obtained after oven drying at a temperature of 60 °C until constant mass. In this study, duplicate samples were tested for each formulation and the mean value is reported as the result. From these data, porosity accessible to water can be calculated as follows:

$$\phi = \frac{M_s - M_D}{M_s - M_w} \quad (2)$$

Even though oven-drying at 105 °C has remained the most widely used technique, some studies [19] suggested that oven drying at this temperature can alter the pore structure and causes some hydrates such as ettringite and CSH, to lose a significant amount of non-evaporable water and therefore produce an overestimation of total porosity. These studies have also shown that the values of water porosity obtained by drying at 60 °C are very similar to those obtained by vacuum drying or by freeze-drying.

Table 2
Proportions of the materials tested.

Mixtures ID	SN. 0%	SN. 10%	SN. 30%	SN. 50%	SN. 55%	SN. 60%	SN. 65%
W/C	0.4	0.4	0.4	0.4	0.4	0.4	0.4
C_{ag}	0%	10%	30%	50%	55%	60%	65%
Gle-27 (%)	–	–	–	–	–	0.5	1.5

W/C is the water-to-cement ratio.
C_{ag} is the relative aggregate volume content.
Gle-27 (%) is the mass of Glenium 27 relative to mass of cement.

2.2.2. Mercury intrusion porosimetry

Before testing, the samples were first frozen (−195 °C) by immersion into liquid nitrogen for 5 min. This quick quenching process occurs at a very low temperature and allows for the generation of ice microcrystals that do not alter the microstructure. After freezing, the samples were introduced for 7 days in a freeze-dryer vacuum at 10^{-1} Pa. This operation allows the ice trapped in the material porosity to sublimate. This technique is considered to be a suitable procedure for the MIP investigation of cement-based materials [19,20]. MIP measurements were performed 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 was approximately 3 nm. For each specimen, two samples were tested and the results were averaged.

2.3. Diffusion tests

2.3.1. Through-out diffusion tests

The through-out diffusion tests consisted of putting the mortar sample between two compartments. The samples were sealed into position using an epoxy adhesive and by means of O-rings to avoid leakage.

Each compartment with a volume of 111 ± 1 ml was filled with saturated lime water. Then the cell was left to stand approximately fifteen days to check the tightness of the cell and stabilize the sample before the test. After this period, the upstream compartment of each cell was doped with tritiated water in the HTO diffusion tests, and with LiCl in the remaining tests. The amount of elements transferred from the upstream to the downstream compartment was then followed in time by successive samplings which were analyzed by an ion chromatography device (for monitoring Li^+ and Cl^- ions), and by a scintillation tritium monitor for the monitoring of HTO. The lower limit of detection for the ion chromatography is 0.18 μmol/L.

During the test, the concentration at the downstream compartment was set to not reach 3% of the upstream concentration. Otherwise, the downstream solution was drained. Therefore, the upstream and downstream concentrations (C_0 and C_1, respectively) were maintained at nominally constant values at all times (($C_0 = 3.2 \times 10^6$ Bq/L; $C_1 \approx 0$) for HTO and ($C_0 = 41$ mmol/L; $C_1 \approx 0$) for LiCl solution).

Table 1
Particle size distribution of the standardized sand used.

Sieve mesh size (mm)	0.08	0.16	0.50	1.00	1.60	2.00
Total amount retained on the sieve (%)	99 ± 1	87 ± 5	67 ± 5	33 ± 5	7 ± 5	0