

# Ionic aqueous diffusion through unsaturated cementitious materials – A comparative study



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## HIGHLIGHTS

- The chloride diffusion coefficient is measured as a function of the saturation level by impedance spectroscopy.
- 4 Types of materials made of Portland cement and blended cement are tested in a saturation level ranging from 0.2–1.
- The evolution of the diffusion coefficient with the saturation level is closely related to the pore size distribution.

## ARTICLE INFO

### Article history:

Received 21 July 2013

Received in revised form 2 October 2013

Accepted 15 October 2013

Available online 8 November 2013

### Keywords:

Cement-based materials

Saturation level

Diffusion coefficient

Impedance spectroscopy

## ABSTRACT

The diffusion coefficient is a highly important parameter either as a durability indicator in the field of civil engineering or as an assessment criterion in the domain of nuclear waste disposal. In this paper we address the fundamental issue of the diffusion coefficient evolution with the water saturation level of cement-based materials. The study is comparing concretes and cement pastes cast with either blended cement or Portland cement. The analysis emphasizes the impact of the pore size distribution on the diffusivity as a function of the saturation degree.

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## 1. Introduction

The mechanism of diffusion through porous media is the ability of a species, ionic or molecular, to move across the porous material when a concentration difference is applied as driving force. This ability can be quantified by a diffusion coefficient, which is a parameter of great importance in several scientific domains. It may allow for instance to assess the suitability of a determined storage solution for nuclear waste disposal. It can also be used to evaluate the durability of a concrete structure vis-à-vis either the corrosion of its reinforcement bars by chloride ion penetration through the concrete cover, or the expansive products generated by sulphate ions entering the material.

The diffusion coefficient is a macroscopic parameter that depends on the characteristics of both the diffusing species and the porous material involved in the diffusion process [1–3]. Thus, the material microstructure, which characteristics ensue both from the properties of the material itself as well as from its history

and environmental conditions, plays a main part when dealing with the diffusion coefficient.

In a recent paper [4], we documented the lack of research works on molecular transport through unsaturated systems (cf. references *ibid.*) and the lack of data establishing a relationship between the diffusion coefficient and the saturation level of porous materials. Moreover, the techniques widely used in civil engineering to measure diffusivity through cementitious materials are suited for fully saturated conditions. These techniques cannot be used when it comes to partially saturated materials for the very reason that they request to place the samples of material between compartments containing solutions at various concentrations. The water content gradients thus created prevent from maintaining the initial saturation level inside the material.

Climent et al. [5], followed by De Vera et al. [6], published a method for measuring the diffusion coefficient of chloride ions through partially saturated concrete, from a natural diffusion test and by means of Fick's second law of diffusion. Guimarães et al. [7] presented another experimental set-up for the natural diffusion test allowing also to calculate the chloride diffusion coefficient through unsaturated concrete using Fick's second law. Ben Fraj et al. [8] proposed a new experimental set-up aiming at character-

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using chloride ingress in non-saturated concrete. Chloride profiles measured when concrete is partially saturated can also be found in [9].

Our group proposed recently an approach to determine the diffusion coefficient of any ionic species through a partially saturated porous medium [4]. This approach was proven effective in the case of a Portland-cement concrete. We could determine experimentally the diffusion coefficient for different saturation levels of the material. This allowed to show the correlation between the diffusion coefficient and both the porous network characteristics (porosity, porosimetry) and the hydric state of the material.

On that basis, the approach is extended in this paper to different types of cementitious materials: a blended-cement (with mineral additions) concrete and the two corresponding cement pastes (Portland and blended). Once the diffusion coefficient in non-saturated conditions is measured, a comparative analysis allows to identify the leading paths for diffusion through the different kinds of material. Besides, a brief review is first made on the validation of the present method, carried out on saturated materials and detailed elsewhere [10], by means of an electrokinetic technique. This review permits to verify the coherence with respect to the non-saturated sample results presented here, and to make some scale effect considerations.

## 2. Materials, characterisation and sampling

Two different kinds of cementitious materials were tested, namely cement paste and concrete. Each of them was prepared using two different varieties of cement: a common Portland one and a blended one (containing mineral additions: flying ashes and blast furnace slag). The composition of both types of concrete was presented before [10]. A water-to-cement ratio of 0.43 and 0.41 was used, respectively. The same ratio was adopted to prepare the two corresponding types of cement pastes. At the end of a curing period of 6 months under controlled conditions (humid chamber, 20 °C), the apparent density and the water porosity of the four types of materials were measured (Table 1).

Mercury intrusion porosimetry tests completed the characterisation of the materials. The pore size distribution of the cement pastes is presented in Fig. 1 and in Fig. 2 for the concretes.

In addition, pore solution extractions were performed on the two types of concrete, and the ionic compositions of these solutions determined. That led to the definition of representative artificial solutions having identical sodium and potassium concentrations and which are in practice equivalent to the pore solutions extracted, especially from an electrochemical point of view. In fact, the presence of calcium and sulphate ions was found to be negligible vis-à-vis the ionic strength due to their very low concentrations. The ionic compositions of the two artificial solutions are shown in Table 2.

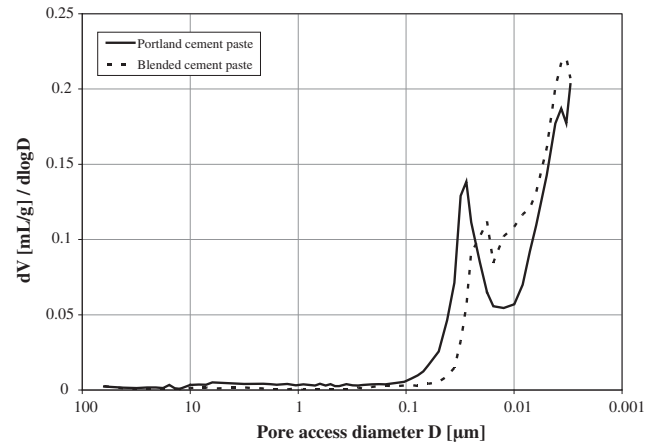
The samples used for this study were disks with a diameter of 28 mm and a thickness of 20 mm. These dimensions were chosen as a compromise between the time needed to reach hydric equilibrium and the largest size of aggregates in concrete. Three samples (coming from three different specimens) of each material were placed inside hermetic containers at 20 °C where supersaturated saline solutions were previously put. Seven relative humidity were tested, i.e. 94%, 84%, 75%, 66%, 55%, 44% and 33%. These values are actually reference ones because the hydric state of the material was characterised by its saturation level. The samples were kept inside the container until hydric equilibrium was reached, before proceeding to impedance measurements. The saturation level of a sample was measured as the ratio between the water volume in its pores and the total volume of its pores, following the AFPC-AFREM protocol [11].

## 3. Experiments – electrochemical impedance spectroscopy (EIS)

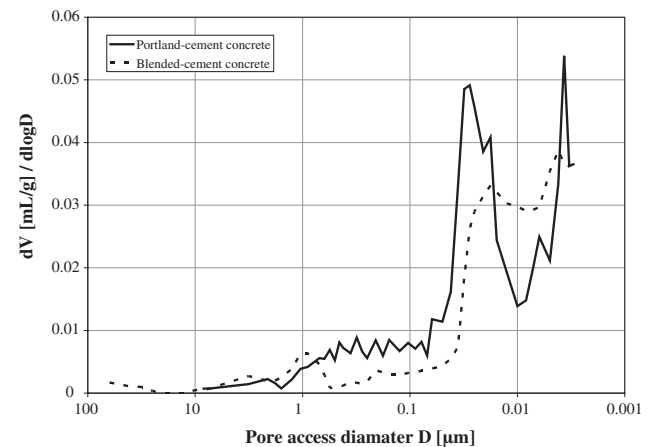
The approach used involves the determination of the electrical ohmic resistance of a given porous medium by means of its imped-

**Table 1**  
Material characteristics.

	Cement	Apparent density (kg m <sup>-3</sup> )	Water porosity
Cement paste	Portland	1580	0.39
	Blended	1594	0.37
Concrete	Portland	2330	0.13
	Blended	2285	0.14



**Fig. 1.** Pore size distribution of the cement pastes.



**Fig. 2.** Pore size distribution of the concretes.

**Table 2**  
Artificial solutions composition.

Solution	Na <sup>+</sup> (mol m <sup>-3</sup> )	K <sup>+</sup>	OH <sup>-</sup>
N° 1 (Portland-cement concrete)	31.5	122.8	154.3
n° 2 (blended-cement concrete)	70.7	173.9	244.6

ance (AC) response. The technique is based on the formation factor  $F_f$  concept [12,13], i.e. the ratio between the electrical conductivity of the pore solution  $\sigma_o$  (S/m) contained in a porous material at a given state, and the conductivity of the material itself  $\sigma_{mat}$  (S/m) at that state. The results obtained in this way needed to be corroborated by means of a well-known test method. On that purpose, an electrokinetic test, based on chloride ions migration under an electrical field, was used. More details on this test can be found elsewhere [10]. This is why the approach described hereafter is used to calculate the diffusion coefficient of chloride ions  $D_{e,Cl^-}$  through a given porous material. Nevertheless, by using the appropriate value of  $D_{o,i}$  in Eq. (4), it may possible to assess any ionic species diffusion coefficient.

The formation factor writes:

$$F_f = \frac{\sigma_o}{\sigma_{mat}} \quad (1)$$

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