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Unsaturated ion diffusion in cementitious materials – The effect of slag and silica fume

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ABSTRACT

This paper investigates the moisture dependency of ion diffusion in binary cementitious binders with Portland cement (OPC) in combination with slag or silica fume. Resistivity measurements and calculations with a thermodynamic model, GEMS, were used to assess the unsaturated chloride diffusion coefficient. The results show that the relation between the relative diffusion coefficient and the degree of saturation is not significantly affected by w/b (in the investigated range of w/b from 0.38 to 0.53), while the investigated binder compositions seem to affect the relation. These results are of value for service-life models, where they potentially represent important input data. The results also highlight the need for considering the pore solution conductivity when using resistivity measurements for evaluation of ion transport properties.

1. Introduction

Most degradation of concrete structures is related to ion transport, which is strongly dependent on the moisture content of the material [1]. To create durable concrete structures, service-life models are used to predict the performance of the material over time. Important data for these service-life models are the unsaturated ion transport properties of the material and their relation to the moisture content and pore structure of the material [2]. The pore structure is changed by the substitution of ordinary Portland cement (OPC) with supplementary cementitious materials (SCMs), and this radically changes the transport properties of the material [3]. The changes in pore structure have received increased attention in research since the use of SCMs, such as ground granulated blast-furnace slag (slag), fly ash (FA) and silica fume (SF), is increasing due to their lower emissions of carbon dioxide. For example, in a recent review of unsaturated transport [4], Zhang and Zhang point out that there is a need for more experimental data on unsaturated transport properties of materials with blended binders. This review [4] also points out that the effect of water to binder ratio (w/b) on diffusive ionic transport needs to be clarified.

To date, there is no generally accepted method to assess the unsaturated ion transport properties of cementitious material. However, the phenomenon has been investigated by using different approaches [4]. A number of studies have used Fick's second law and assessed the chloride diffusion coefficient from obtained chloride profiles in unsaturated specimens [5–8], but such use of Fick's second law is questionable. In some of these studies, binding of chlorides is taken into account [7,8]. Other studies have evaluated the chloride diffusion coefficient through measurements with impedance spectroscopy and the Nernst-Einstein equation. For example, a study by Buchwald [9] shows how the degree of saturation affects the ionic transport in masonry materials. In a study by Francy on cement and mortar [10], the evaluated diffusion coefficient as a function of degree of saturation is used for modeling chloride ingress in unsaturated mortar specimens, and it is concluded that it is crucial to divide the total moisture transport into one part that contributes to ion transport and one part that does not. If not, the results can be very misleading. These results are confirmed in a study by Nilsson [11]. Taken together, the work by Francy and Nilsson underlines the importance of input data for modeling and the need for new input data when binders are changed.

In other studies [12–15], resistivity has been used to assess unsaturated transport properties. Larsen et al. [12] have investigated the relation between the resistivity and moisture content of the material. They related their results to the potential corrosion rate of reinforcement, and not to ionic diffusion. Additionally, they pointed out that further interpretation of the data in terms of ionic diffusion is challenging since such interpretation needs to take into account the moisture content of the material and the conductivity of pore solution. Olsson et al. [13] partly solved this challenge by using resistivity measurements and the Nernst-Einstein equation to assess the

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Table 1
Composition of mortars. Quantities are given in kg/m^3.

Mortar label	OPC 0.38	5% SF 0.38	40% slag 0.38	70% slag 0.38	OPC 0.53	5% SF 0.53	40% slag 0.53	70% slag 0.53
Cement/SCM	100/0	95/5	60/40	30/70	100/0	95/5	60/40	30/70
w/b	0.380	0.381	0.391	0.386	0.530	0.531	0.539	0.545
Cement	516	406	308	153	436	484	260	129
Slag	–	–	206	357	–	–	174	302
Silica fume	–	21	–	–	–	25	–	–
Water	196	204	198	200	231	239	234	235
Normsand (EN 196-1)	1548	1607	1543	1531	1525	1574	1519	1508
Plastisizer	1.18	1.06	0.94	0.96	–	–	–	–

unsaturated chloride diffusion coefficient for OPC mortars. However, the study did not assess the chloride diffusion coefficient for blended binders.

In the present paper, the unsaturated chloride diffusion coefficient is presented for OPC and binary cements with slag or SF. As in the study by Olsson et al. [13], resistivity measurements and the Nernst-Einstein equation are used. In this paper, in contrast, the composition of the pore solution is determined through thermodynamic modeling using the Gibbs free energy minimization program GEMS. Pore solution extraction was used for verification of the pore solution compositions predicted by GEMS. This approach enables the evaluation of unsaturated ion transport properties for blended binders. The moisture dependency of the ion transport properties is discussed in relation to different moisture potentials: relative humidity (RH), degree of saturation (S) and moisture content (w). The effect of water to binder ratio (w/b) and the possibilities of using the data when modeling are also discussed.

2. Materials

In this study, eight mortars with two w/b and four binders were used. The composition of the mortars and the raw materials are given in Table 1 and Table 2, respectively. The samples were wet cured for three months and then step-wise conditioned to a series of RHs during one year. This means that moisture state of all samples is on the first desorption isotherm, i.e. the samples have not been dried below the moisture state where they are measured. The samples used are the same as previously reported, and the details on sample preparation are given in [13]. It should be mentioned, though, that in this study, the dry state is defined as the condition of samples equilibrated to 11% RH at 20 °C. The reason for this is that further drying removes chemically bound water which might change the pore structure [16,17].

Mortars for pore solution extraction were prepared separately. The composition of the mortars and their raw materials are similar to the other samples, with the exception that the samples for pore solution extraction were sealed cured at a temperature of 20 °C.

3. Methods

Chloride diffusion coefficients have been assessed with the Nernst-Einstein equation (Eq. (1)), as previously reported [13,18]. The Nernst-Einstein equation is given by:

$$\sigma/\sigma_0 = D_i/D_{0i}, \tag{1}$$

where σ (S/m) is the conductivity of the bulk material, σ_0 (S/m) is the conductivity of the pore solution, D_i (m^2/s) is the calculated diffusion coefficient for ion i in the bulk material, and D_{0i} (m^2/s) is the diffusion coefficient of ion i in pore solution. For chloride ions, D_0 equals 1.483–1.484 × 10^{-9} m^2/s in electrolytes within the range 0.1–1.0 mol/l [19]. The assessed diffusion coefficient does not include the interaction of ions with the binder.

3.1. Resistivity of bulk material and desorption isotherms

The resistivity of the bulk material was determined with direct current and with one electrode covering each side of the sample. When direct current is used, there is a risk for errors due to polarization which results in an underestimated resistance of the material, and when altering current is used the measured resistance shows a frequency dependence [20]. In this study, measurements were taken as quickly as possible to reduce the effect of polarization. The desorption isotherms were assessed with a gravimetric method using climate boxes. The degree of saturation, S (−), at a specified relative humidity, RH (%), is defined as

$$S = w(RH)/w(100\%) \tag{2}$$

where w(RH) (kg/m^3) is the amount of water in the material at relative humidity RH and w(100%) (kg/m^3) is the amount of water in the material at capillary saturation. Capillary saturation is defined as the moisture content of the wet cured specimens after one year and three months wet curing. The resistivity of the bulk material and the desorption isotherms used in the calculations were adopted from [13]. Though, in this study, the desorption isotherms were assessed by use of the dry mass as the mass of samples conditioned to 11% RH and 20 °C. The present paper includes new results from resistivity measurements on samples conditioned to 33% RH. These measurements were performed according to [13].

3.2. Prediction of conductivity of pore solution

To assess the conductivity of pore solutions, thermodynamic calculations has been used for prediction of the chemical composition and ionic concentration of pore solutions. The results from the thermodynamic calculations were verified with measured pore solution compositions form pore solution extraction.

Pore solution extraction was used for determination of the chemical composition of pore solutions at the age of one month. The results from these measurements were used only for verification of the pore solution compositions predicted by GEMS. Pore solution extraction method can be difficult in cases of materials with low w/b and with old materials since in these cases no solution can be extracted. The age of one month was chosen to have samples young enough to be able to extract pore solution, and still old enough to get an estimation of pore solution composition at an age comparable to the age of resistivity measurements. The mortar samples for pore solution extraction were cured for one month in a closed PE container to avoid water loss and to minimize CO_2 uptake. The pore solution was extracted from the samples with a high pressure steel die. The solution was filtered with a 0.45 µm cellulose acetate filter. A syringe was used for the collection of pore solution to minimize the risk of carbonation of the extracted solution. The sodium and potassium concentration of pore solution was then measured with inductively coupled plasma optical emission spectrometry, ICP-OES.

The pore solution composition at saturation was also calculated using thermodynamic modeling using GEMS, a thermodynamic