Construction and Building Materials 145 (2017) 157–165

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Pore structure description of mortars containing ground granulated blast-furnace slag by mercury intrusion porosimetry and dynamic vapour sorption

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HIGHLIGHTS

- DVS and MIP tests are sensitive to pore size distribution changes over time.
- Differences in DVS and MIP results are expected given their different approaches.
- Consideration of the techniques limitations leads to a comprehensive analysis.
- Restrictive pore sizes greatly influence the accessibility into the matrix.
- Pore connectivity has more influence on the test results than pore volume.

ARTICLE INFO

Article history:
Received 25 May 2016
Received in revised form 28 March 2017
Accepted 31 March 2017

Keywords:
Supplementary cementitious materials
Mercury intrusion porosimetry
Dynamic vapour sorption
Ground granulated blast-furnace slag
Porosity
Pore connectivity

ABSTRACT

The description of the pore structure is a key aspect when studying the durability of cement-based materials. Many techniques have been developed over the years in order to describe the actual complex microstructure of these materials. These techniques can be useful to determine the change in pore structure when supplementary cementitious materials are used and also track its evolution with time. This paper particularly aims to describe the changes in the pore structure of mortars with contents of 20, 40 and 60% of ground-granulated blast-furnace slag (GGBFS) in replacement of cement, at the ages of 28 and 90 days. Two widely accepted techniques were applied: dynamic water vapour sorption (DVS) and mercury intrusion porosimetry (MIP). For the data analysis from the DVS test, the Barret-Joyner-Halenda (BJH) model was used for pore size distribution assessment. Moreover, since the extent of this model does not cover the smallest range of pores, calculations with the Dubinin-Radushkevich (DR) model were also made. Results from the MIP test were used to characterize the threshold diameter, the smallest intrudable diameter, and the intrudable porosity. GGBFS replacement leads to a slight increase in porosity values at 28 days, especially seen in the DVS results for the pore size range of 0.002–0.05 μm. DVS results at 90 days for the mix with 40% slag replacement showed a marked reduction in porosity and a shift in pore structure to the finer pore size range when compared to the 28 day results. For all cases, the total porosity was found to be less influential on the test results than pore connectivity.

1. Introduction

Description of the pore structure immediately outlines several other properties, since the pore structure has a great influence on the physical, mechanical and durability behaviours. When supplementary cementitious materials (SCMs) are used, changes in pore structure normally occur over time and in relation to the reaction degree of the SCM, with consequential modifications of the above-mentioned properties. Particularly, the use of ground granulated blast-furnace slag (GGBFS) generally implies an improvement in durability-related properties [1–3]. GGBFS shows both a cementitious nature and pozzolanic activity, i.e. a reaction in the presence of lime [4]. The combination of these effects normally leads to a pore volume reduction with time [1,2,5–7]. In addition, given that GGBFS is a by-product of the steel industry,

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http://dx.doi.org/10.1016/j.conbuildmat.2017.03.245
0950-0618/

its use also helps to reduce clinker production (one of the major sources of CO_2 emissions), which provides an added value to this by-product.

Much effort has been invested in accurately describing the pore structure of cementitious materials [8–13], however, no model or method has been universally acknowledged for providing a complete description and characterization. Nevertheless, limitations do not impede that important information can be obtained from the different current experimental techniques, which may be used as input for analytical models. In this sense, it is important not to forget the critical assumptions made for each method, and to keep a reasonable perspective of the obtained results for their application.

The dynamic vapour sorption (DVS) test provides information regarding pore structure through an experimental set-up to measure the equilibrium between the mass water content of the sample and the relative humidity (RH), at a constant temperature. Several authors [8,12–14] have pointed out some benefits of the use of water sorption instead of other gases for sorption techniques. One of those advantages is that water molecules are relatively smaller than CO_2 or N_2 [8], which allows them to penetrate not only the small sized pores but also into the so-called ink bottle pores. Moreover, it is not necessary to degas the sample prior to the measurements, hence avoiding possible microstructural damage. Furthermore, the test can be performed at room temperature, which is of course quite convenient since there is no need for a major temperature-conditioning equipment. Nonetheless, there are some limitations in the theories of adsorption which mathematically describe the results. For instance, the monolayer is a fictional quantity and not a physical reality as the BET theory implies that the surface is never completely covered until the saturated vapour pressure is reached [15]. Furthermore, calculations of the pore size distribution also have theoretical assumptions, such as the consideration of cylindrical pore shapes [16]. In spite of these limitations, quantitative information can be obtained from the isotherms, which is then used to calculate specific surface area and pore size distribution.

The mercury intrusion porosimetry (MIP) test has been widely used to analyse the microstructure of cementitious materials [13,17–20]. Nevertheless, its interpretation also requires some assumptions and theoretical simplifications, such as the same accessibility to the external surface of all the pores, cylindrical-shaped pores, and absence of ink-bottle pores, all of which vary from the actual pore structures of cementitious materials. Diamond [21] has described these -and other-drawbacks fairly well, but nevertheless still accepted the use of the threshold diameter (d_{th}) and intrudable pore volume (ϕ_{in}) as indexes of the pore structure for qualitative comparison. In fact, from experimental results, three main features have been described to be the most-representative and most-useful for modelling [22]: the intrudable porosity (ϕ_{in}), the smallest intrudable pore diameter (d_{min}), and the threshold pore diameter (d_{th}). It has been clearly stated that ϕ_{in} should not be associated with the total porosity [21–23], but rather with the accessible porosity, as it is equivalent to the volume of mercury intruded corresponding to the highest point in each cumulative curve. On the other hand, the precise determination of d_{th} is controversial. Aligizaki [23] described it as the diameter above which there is comparatively little mercury intrusion, and immediately below which starts a vast intrusion of mercury. In order to objectively assess the value of d_{th}, several authors [22,24,25] have established some methods to provide comparable results. Those methods are described, used, and discussed later in this paper to compare the different obtained values.

In order to convey a comprehensive description of pore structure, mortars with 20, 40 and 60% w/w of GGBFS as replacement of Portland cement were tested at different ages using the DVS and the MIP tests. This paper discusses the data obtained considering the theoretical assumptions of each technique, and describes the pore structure of mortars in the presence of GGBFS and its evolution over time.

2. Materials and methods

In order to perform the tests, three mortar mixes were designed with a water/binder (w/b) ratio of 0.45 and a sand/binder (s/b) ratio of 3. The mixes were designated as S20, S40 and S60, having respectively 20, 40 and 60% w/w of GGBFS with respect to total binder content. The mixing procedure and the compressive strength test were performed in accordance with EN 196-1 [26]. Mortar samples were cured in a humid chamber at 20 ± 2 °C and 95 ± 5% RH for 28 and 90 days, and then conditioned for testing. Water absorption (WA), apparent density, open porosity, and resistivity in the saturated state were determined at 90 days. Compressive strength was measured at 28 days.

For the determination of the apparent density and open porosity, samples were first submitted to a vacuum for two hours and then water was drawn into the vacuum chamber until the sample became fully immersed. After 24 h the sample was removed and weighed, which was denoted as saturated mass in air (m_{sa}). The samples were also weighed in water, and denoted as saturated mass in water (m_{sw}). Then, samples were subjected to drying in an oven at 50 °C until the change in mass was lower than 0.1% in a 24 h period, and denoted as dry mass (m_d). The apparent density was calculated as the ratio between m_d and ($m_{sw} - m_d$), multiplied by the density of water. The open porosity was calculated as ($m_{sa} - m_d$)/($m_{sa} - m_{sw}$). In this paper, total porosity of concrete was linked to the water-permeable or open porosity. This is in fact a simplification (in reality, pores that are not connected to the exterior are not considered in the water-permeable porosity), but this accessible porosity is the responsible for transport mechanisms. Table 1 shows the results of the mentioned tests.

Ordinary Portland cement (OPC) type CEM I 52.5, normalized siliceous sand (0/2) and tap water were used in all mixes. The chemical compositions of the OPC and the GGBFS are shown in Table 2. The particle size distributions of the OPC and GGBFS (Table 3) were determined by means of laser diffractometry using a Malvern Mastersizer 2000 E particle analyser with wet unit Hydro 2000SM. Values of refraction index (n) and absorption coefficient (k) shown in Table 3 were selected according to the values found in literature [27,28] and tested to select the ones which had the best fit and lowest weighed residual to the obtained data.

2.1. Mercury intrusion porosimetry (MIP) test

MIP tests were performed on samples of approximately 1.5 cm^3. A Pascal 440 mercury porosimeter with a maximum load capacity of 420 MPa was used. However, the maximum pressure was limited to 200 MPa in order to avoid cracks induced by the mercury pressure [29]. The adopted mercury surface tension and contact angle between the mercury and the solid surface were 482 mN/m and 142°, respectively. A blank run for differential mercury compression was made to correct the volume measurements [18]. The pore diameters related to the pressure applied were calculated with the Washburn equation [30].

To minimize microstructural damage during pre-conditioning, samples were first dried at 40 °C for 24 h, and then vacuum-dried at 20 ± 2 °C for two weeks at 0.1 bar. This preconditioning technique has been validated through microstructural analyses in previous studies [14,31].

The data obtained from the MIP test was used to determine d_{min}, ϕ_{in}, and d_{th}. The calculation of d_{th} was made considering two methods:

i) the 5% method: this method was used by [24], where d_{th} is calculated as the point in which the porosity is 5% of ϕ_{in}. This offers the advantage of a conventional value and protocol, since there is no need to assume at which point sufficient mercury has penetrated into the porous system. The d_{th} obtained by using this method has been denoted as d_{th} (5%).
ii) the tangent method: this method was first adopted by Liu and Winslow [25] to determine the threshold diameter as that corresponding to the intersection of tangent lines on the cumulative distribution curve at the smallest diameter that did not exhibit significant intrusion and the largest diameter that did. Using this approach as a basis, Ma [22] fitted points at

Table 1
Properties of mortars (mean ± standard deviation).

Mixes	S20	S40	S60
Compressive strength (MPa)[28 d]	75.0 ± 1.2	56.0 ± 1.6	49.0 ± 1.6
Compressive strength (MPa)[90 d]	75.4 ± 0.9	61.2 ± 1.7	54.1 ± 1.6
Water absorption (%)[90 d]	5.9 ± 0.4	6.7 ± 0.2	7.0 ± 0.2
Apparent density (g/cm^3)[90 d]	2.50 ± 0.02	2.55 ± 0.01	2.55 ± 0.04
Porosity (%)[90 d]	12.8 ± 0.8	14.5 ± 0.4	15.1 ± 0.5
Saturated resistivity (kohm·cm) [90 d]	20.64 ± 1.2	23.08 ± 0.8	29.68 ± 2.3