PREPRINT VERSION

Determination of the hygric properties of the heritage stone of the Cathedral of Cuenca through the water absorption by capillarity test

Virginia Cabrera, Ángel Yustres*, Rubén López-Vizcaíno*, Oscar Merlo, Miguel Ángel Ruiz, Enrique Torrero, Vicente Navarro

Institute of Technology, Universidad de Castilla-La Mancha, Campus Universitario s/n,
16071 Cuenca, Spain.

Corresponding Authors* ruben.lopezvizcaino@uclm.es; angel.yustres@uclm.es,
Institute of Technology, Universidad de Castilla-La Mancha, Campus Universitario s/n,
16071 Cuenca, Spain. Tel. 926 29 53 00 Fax 926 29 53 01

FULL VERSION HERE:

<https://doi.org/10.1016/j.culher.2020.11.009>

SUPPLEMENTARY MATERIAL:

<https://ars.els-cdn.com/content/image/1-s2.0-S1296207420305057-mmc1.docx>

ABSTRACT

This work analyses the characterization of the hygric behaviour of a stone heritage material by solving the inverse problem using experimental data obtained from a water absorption by capillarity test (EN 15801). This common test is undemanding and requires relatively simple equipment as compared to other hygric characterization tests. For the solution of the direct problem of transient flow in partially saturated porous media, a computational module was developed in COMSOL Multiphysics that includes the conceptual model from the standard EN 15026. The selected material was the heritage stone of the Cuenca Cathedral, differentiating between two characteristic lithotypes: one with greater porosity and another that is more resistant, with more reduced porosity. Based on the experimental results, the intrinsic permeability and the parameters of the moisture storage function are estimated for the two lithotypes. Similarly, contrast tests were conducted to quantify the estimation error. A stochastic analysis was performed to assess if the estimated hygric parameters satisfactorily characterize the behaviour of the studied stone.

KEYWORDS

Heritage stone; water absorption; capillarity; inverse problem; hygric characterization

1. INTRODUCTION

The architectural heritage of the declared UNESCO World Heritage Cities makes up a significant part of the material elements that offer a better understanding of what was and continues to be the history of humanity [1]. Therefore, its preservation, maintenance and rehabilitation are some of our greatest social responsibilities. Among all of the elements making up the architectural heritage, the stone materials used in its construction play one of the most important roles in preservation actions. To a large part, heritage stone (HS) pathology is caused by phenomena generated by the transport of water inside the material [2-6]. Therefore, the hygric characterization of this material is essential to carry out preservation and rehabilitation actions [7, 8]. In Spain, this has resulted in the standard UNE 41810 [9]. Similarly, the European standard EN 16515 [10] establishes the tests for a complete characterization of the HS. Specifically, the hygric properties within the aforementioned framework are determined, among others [11], through the water absorption by capillarity (WAC) test according to EN 15801 [12], the water vapour permeability (WVP) test by EN 15803 [13], and the drying properties (DP) test according to EN 16322 [14]. These tests are undemanding and do not require costly experimental or analytic equipment. Abundant examples of HS characterization can be found in the literature [15-19]. However, these tests are intended to obtain performance indexes rather than material parameters of conceptual models for the simulation of water transport by the use of numerical tools [5, 20-23]. Procedures aimed at obtaining these material parameters directly are available, but they generally require the use of very specific equipment not easily available. To avoid this limitation, alternative strategies for estimating material parameters using data provided by standardized tests [12-14] should be considered.

2. RESEARCH AIM

The objective of this work is the development of a methodology that allows the estimation of the parameters of water flow (intrinsic permeability and moisture storage function) in HS through conventional hygric characterization tests, with a low technical, economic and time cost and with acceptable quality.

The WAC test has been selected as a reference test. This is a suitable test for the study of water flow since it involves water transport processes in both the liquid and gas phase in unsaturated porous media. The selected material was the limestone used in the construction of the Cathedral of Santa María and San Julián in the city of Cuenca (Spain) [24]. The estimation of the material parameters was based on a code for the modelling of flow in partially saturated porous media under transient conditions developed by the authors in the multiphysics implementation platform COMSOL [25]. The conceptual model used in standard EN 15026 [26] was adopted. Besides, stochastic analysis of the sensitivity of the model was carried out, which allowed the validity of the proposed methodology to be evaluated.

3. MATERIALS AND METHODS

3.1 Limestone

As mentioned above and to inspect its scope, the proposed formulation has been applied to analyse the behaviour of the limestone used in the construction of the Cathedral of Santa María and San Julián of Cuenca (Spain).

The samples were extracted from the quarry located in Arcos de la Cantera (Cuenca, Spain) and two different lithotypes were identified: (i) the Porous Heritage Stone (PHS), used in ornamental elements, and (ii) the Compact Heritage Stone (CHS), used in structural elements [28].

The mineralogical characterization performed via X-ray diffraction technique is presented in the supplementary material (see Table SM1 and Figure SM1). In both lithotypes, calcite is the predominant mineral. The CHS also contains a significant fraction of quartz (Q peak in Figure SM1b). The real density is 2746 and 2623 kg m⁻³ and the apparent density is 1498 and 1886 kg m⁻³, respectively for PHS and CHS [29]. A detailed characterization of both lithotypes can be found in [28]. Figure 1 shows a picture of the analysed samples and a WAC test in progress, conducted following the EN 15801 standard.

Figure 1. (a) PHS Sample, (b) CHS and (c) WAC test.

3.2 Hygric characterization test: WAC test

The WAC test assesses the increase in the adsorbed water mass over time in a cubical sample (50×50×50 mm in the present work) of material placed on a saturated permeable bed. The slope of the initial zone of the curve resulting from the graphical representation of the experimental water absorbed per surface unit (Q) against the square root of time defines the WAC coefficient, (slope of the straight lines in Figure 2). According to the standard EN 15801, this coefficient synthesizes the information obtained from the test.

In the present work, 22 samples were tested for the PHS lithotype and 20 samples for the CHS, obtaining the results shown in Figure 2, where the WAC coefficients are presented

89 in Table SM2. The tests lasted until a steady-state mass was reached and, consequently,
 90 the duration depended on the nature of the lithotype, longer for CHS and shorter for PHS,
 91 since the hydraulic conductivity was lower for the former and higher for the latter.

92

93 **Figure 2.** WAC experimental data. (1) PHS and (2) CHS. Samples: (a) to (d).

Figure 3 shows the dispersion of the WAC coefficients. The mean value for PHS is 0.92 kg m⁻² s^{-1/2} (coefficient of variation, CV = 17.93 %) and in the case of CHS, it is 0.12 kg m⁻² s^{-1/2} (CV = 27.74%). The box-and-whisker plot of the WAC coefficient has an outlier point for PHS corresponding to test 4.

Figure 3. Box-and-whisker plot of WAC coefficient. Grey, PHS samples and white, CHS samples.

3.3 Qualification test: Hydraulic conductivity in a saturated condition test

As mentioned previously, the WAC tests are designed to obtain only the absorption coefficient by capillarity, and not to estimate any other material parameters. Therefore, an inspection exercise was performed to assess the reliability of the proposed methodology by analysing the quality of the estimated parameters. These qualifications tests were performed using a flexible-wall permeameter to determine of the hydraulic conductivity in saturated condition by the standard ASTM D5084–16a [27]. This test is based on the application of a constant and controlled hydraulic gradient over the sample, having a similar arrangement to that presented in Figure 4. It is possible to determine the saturated hydraulic conductivity, K_{sat} [m s⁻¹], using the values of the piezometric heads applied and the water flow in the sample under saturated conditions and Darcy's law given by the expression

$$q = -K_{sat} \nabla h \quad (1)$$

where q is the water flow [m s^{-1}] and ∇h is the gradient of the piezometric head (dimensionless).

Figure 4. Layout of the saturated hydraulic conductivity test apparatus. (A) Sample, (B) Porous disc, (C) Membrane, (D) Confining chamber, (E) Water inlet and (F) Water outlet.

Ten cylindrical samples were tested (25 mm height, 50 mm diameter) for each lithotype. Table 1 shows the results obtained for each sample of both lithotypes.

Table 1. Saturated hydraulic conductivity of each sample.

PHS sample	$K_{\text{sat}} (\text{m s}^{-1})$	CHS sample	$K_{\text{sat}} (\text{m s}^{-1})$
1	1.17×10^{-6}	1	8.47×10^{-8}
2	1.40×10^{-6}	2	8.95×10^{-8}
3	2.05×10^{-6}	3	8.20×10^{-8}
4	1.82×10^{-6}	4	1.20×10^{-7}
5	1.45×10^{-6}	5	8.66×10^{-8}
6	1.39×10^{-6}	6	7.63×10^{-8}
7	1.40×10^{-6}	7	8.36×10^{-8}
8	1.31×10^{-6}	8	7.84×10^{-8}
9	1.34×10^{-6}	9	1.08×10^{-7}
10	1.56×10^{-6}	10	8.58×10^{-8}
Mean	1.49×10^{-6}	Mean	8.59×10^{-8}
Standard deviation	2.61×10^{-7}	Standard deviation	1.38×10^{-8}
CV* (%)	1.22	CV* (%)	0.87

* Coefficient of variation of the logarithm of K_{sat}

4. CONCEPTUAL MODEL AND IMPLEMENTATION

4.1 Conceptual model

In the simulation of the WAC test, one-dimensional and isothermal (average temperature of 23° C) flow of water was assumed, also ensuring that the gas pressure, P_G , was kept constant and equal to the atmospheric pressure. Besides, it was considered that the material is non-deformable. The conceptual model selected was based on that described in the standard EN 15026 [26]. In this way, the balance of the water mass in the sample, without considering water sources or sinks in the domain, can be given by the expression

$$\frac{\partial w}{\partial t} + \nabla \mathbf{g} = 0 \quad (2)$$

where w is the moisture content per total volume unit [kg m^{-3}], $\mathbf{g}$ is the moisture flow rate [$\text{kg m}^{-2} \text{s}^{-1}$] and $\nabla \cdot$ is the divergence differential operator.

The moisture content term considers the contributions of the liquid, w_w , and vapour, w_v , phases by the following expression

$$w = w_w + w_v = \phi Sr \rho_w + \phi(1 - Sr) \rho_v \quad (3)$$

where ϕ is the porosity [$\text{m}^3 \text{m}^{-3}$], Sr is the degree of saturation [$\text{m}^3 \text{m}^{-3}$], ρ_w is the liquid water density [kg m^{-3}] and ρ_v is the water vapour density [kg m^{-3}] (see Appendix B). The moisture flow rate, $\mathbf{g}$, is obtained from the contributions of the liquid, $\mathbf{g}_w$, and vapour, $\mathbf{g}_v$, phases as pointed out by Cabrera et al [30]

$$\mathbf{g} = \mathbf{g}_w + \mathbf{g}_v = k \nabla S + \delta_p \nabla P_v \quad (4)$$

where k is the liquid conductivity [s], δ_p is the vapour permeability [$\text{kg Pa}^{-1}\text{m}^{-1}\text{s}^{-1}$] s is the matric suction [Pa], P_v is the water vapour pressure [Pa] and ∇ is the gradient operator. The vapour pressure is calculated using the psychrometric equation (Appendix B). The matric suction, state variable of the model, is identified with the capillary suction, $s = P_G - P_L$, where P_L is the liquid pressure. The liquid conductivity has been calculated as

$$k = \frac{\kappa K_{\text{int}}}{\mu_w} \rho_w \quad (5)$$

where K_{int} is the intrinsic permeability [m^2], μ_w is the dynamic viscosity of the water (equal to $9.26 \times 10^{-5} \text{ N s m}^{-2}$ at 23° C , [31]) and κ is the relative permeability [dimensionless]. The relative permeability has been determined using the van Genuchten [32]-Mualem [33] approach

$$\kappa = Sr^{\frac{1}{2}} \left[1 - \left(1 - Sr^{\frac{1}{m}} \right)^m \right]^2 \quad (6)$$

where m is a model parameter [dimensionless] and Sr is the degree of saturation, which is estimated by the van Genuchten water retention curve (WRC), function selected to define the moisture storage in the material, also considered for several authors [34-36], it is given by the expression

$$Sr = \left(1 + (\alpha s)^n \right)^{-m} \quad (7)$$

where α [Pa^{-1}] and n [dimensionless] are model parameters. The consistency of using the van Genuchten [32]-Mualem [33] approach to defining the relative permeability and the WRC of the selected limestone was positively tested in previous work [30]. The vapour permeability is given by

$$\delta_p = \frac{\delta_0}{\mu} \quad (8)$$

where δ_0 is the vapour permeability of the still air [$\text{kg Pa}^{-1}\text{m}^{-1}\text{s}^{-1}$] and the dimensionless diffusional resistance factor μ is calculated as [37]

$$\mu = \frac{1}{\tau_v \phi (1 - Sr)} \quad (9)$$

where τ_v [dimensionless] is the tortuosity and is considered equal to 1 [38]. Finally, the vapour permeability of the still air is given by the expression calculated as

$$\delta_0 = \frac{D_v MM_w}{R T} \quad (10)$$

where R is the ideal gas constant [$\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$], T is the absolute temperature [K], MM_w is the molar mass of water [kg mol^{-1}], and D_v is the binary diffusion coefficient of the water vapour [$\text{m}^2 \text{s}^{-1}$], which is given by the expression [37]

$$D_v = 5.9 \times 10^{-6} \frac{T^{2.3}}{P_G} \quad (11)$$

4.2 Numerical implementation

A moisture transfer module was implemented in COMSOL Multiphysics [25], a partial differential equation implementation platform based on the application of the finite element method with Lagrange multipliers. The moisture transfer module was verified and validated, obtaining positive results in previous work [30]. To simulate the WAC test, the one-dimensional system depicted in Figure 5 was assumed. The samples were kept in a controlled relative humidity (RH) of 32% to have a homogeneous initial suction and that was easily calculable through the psychrometric law (Equation B2). The bottom boundary corresponds to the base of the sample, in close contact with the saturated permeable layer. Consequently, a Dirichlet condition ($s = 0 \text{ Pa}$) has been imposed on this

boundary. The top boundary condition was defined by the formulation described in EN 15026 for moisture transport across the interfaces (material-environment).

Figure 5. Scheme of discretization: Boundary and initial conditions.

For the inverse problem analysis, COMSOL Multiphysics Optimization Module was coupled with the moisture transfer module developed by the authors [30]. The total mass of water contained in the sample, $w_{\text{tot,cal}}$, is compared with the value obtained experimentally, $w_{\text{tot,obs}}$. A least-squares objective function was adopted and the Nelder-Mead method [39] was selected for the minimization problem.

5. RESULTS AND DISCUSSION

5.1 Parameter estimation

The material parameters of the conceptual model adopted are porosity, ϕ , intrinsic permeability, K , and the parameters α , n y m of the van Genuchten WRC. However, only K , n and m were estimated, since ϕ and α may be calculated based on the experimental results obtained in the correspondent WAC test.

To calculate accessible porosity, it is necessary to know the volume of accessible voids in the sample. Since the WAC test ends when there are no further increase in the sample mass is observed, at this point, the accessible voids are almost at saturated conditions, and it may be assumed that the volume of the accessible pores, V_v , is equal to the volume of

203 the water contained in the material, V_w^{sat} . This volume may be calculated using the
 204 expression:

$$205 \quad V_v = V_w^{\text{sat}} = \frac{m_{\text{sat}} - m_{\text{dry}}}{\rho_w} \quad (12)$$

206 where m_{sat} corresponds to the mass of the sample when the steady-state has been reached
 207 and m_{dry} is the completely dry sample (a value that is easily measured by oven drying
 208 before conditioning the WAC test). Once the V_v value is known, the accessible porosity
 209 ϕ may be calculated as

$$210 \quad \phi = \frac{V_v}{V_T} \quad (13)$$

211 where V_T is the total volume of the sample. The accessible porosity of each of the sample
 212 is shown in Table SM3.

213 The parameter α is calculated for each sample using the equation derived from the van
 214 Genuchten approach

$$215 \quad \alpha = \frac{1}{s_o} \left[\left(\frac{1}{Sr_o} \right)^{\frac{1}{m}} - 1 \right]^{\frac{1}{n}} \quad (14)$$

216 where n and m are obtained in the estimation process, s_o is the initial suction
 217 corresponding to the RH which is equilibrated with the sample at the start of the WAC
 218 test and Sr_o is the degree of saturation of the sample at this moment, obtained from the
 219 moisture content expression, Eq. (3)

$$220 \quad Sr_o = \frac{w_o - \phi \rho_v}{\phi(\rho_w - \rho_v)} \quad (15)$$

where w_o , the moisture content at the start of the WAC test, was calculated as

$$w_o = \frac{m_o - m_{dry}}{V_T}$$

m_o being the initial mass of water. Sr_o and w_o values are included in Table SM4.

In Figure 6, the evolution of the water mass of the samples from the WAC test was compared with the model results. It may be observed that the numerical model satisfactorily reproduces the hygric behaviour of the samples. The estimated values of K_{int} , n and m for each sample are shown in Table 2, showing Figure 7 a box-and-whisker plot of the inverse analysis results. For the CHS, the mean values of the K_{int} , n and m parameters are 1.11×10^{-13} , 0.8265 and 0.7357, with a CV of 1.13%, 15.07% and 8.18%, respectively. Similarly, for the PHS lithotype, the mean values obtained for the K_{int} , n and m parameters are 7.92×10^{-15} , 0.06318 and 0.6068, with CV values of 0.85%, 13.27% and 9.80%, respectively. It is important to highlight that, in all cases, the CV obtained is lower than that reached in the determination of the WAC coefficient (see Table SM2). This indicates that the material parameters have a lower dispersion than that of the phenomenological coefficient, and therefore, a better characterization of the material is obtained. Comparing the mean values obtained for each of the two examined lithotypes, it is found that the PHS lithotype has an intrinsic permeability that is two orders of magnitude higher than the one obtained for the CHS, as it was expected, given that CHS is a denser material.

Figure 6. Water mass evolution. Markers, experimental data; solid line, numerical results. (1) PHS and (2) CHS. Samples: (a) to (d).

245 **Table 2.** Estimated hygric parameters of samples.

PHS sample	$K_{int} (m^2)$	$n (-)$	$m (-)$	CHS sample	$K_{int} (m^2)$	$n (-)$	$m (-)$
1	1.14×10^{-13}	0.6433	0.8518	1	8.38×10^{-15}	0.6250	0.6587
2	1.12×10^{-13}	0.8405	0.7175	2	7.94×10^{-15}	0.6821	0.5777
3	1.28×10^{-13}	0.6232	0.8891	3	1.03×10^{-14}	0.7855	0.4893
4	3.92×10^{-14}	0.5839	0.7354	4	8.79×10^{-15}	0.7193	0.5848
5	1.80×10^{-13}	0.8107	0.7770	5	7.89×10^{-15}	0.5768	0.6656
6	9.25×10^{-14}	0.8727	0.7494	6	8.22×10^{-15}	0.6357	0.6551
7	1.35×10^{-13}	0.8278	0.6943	7	5.45×10^{-15}	0.6008	0.6100
8	1.02×10^{-13}	0.8369	0.8021	8	9.31×10^{-15}	0.5955	0.6089
9	1.01×10^{-13}	0.7764	0.7223	9	8.45×10^{-15}	0.7008	0.5942
10	9.64×10^{-14}	0.8248	0.7547	10	8.04×10^{-15}	0.6403	0.6425
11	8.85×10^{-14}	0.6105	0.7025	11	5.78×10^{-15}	0.4956	0.6676
12	9.79×10^{-14}	0.6676	0.6385	12	5.47×10^{-15}	0.5002	0.6647
13	1.46×10^{-13}	0.9220	0.7262	13	1.21×10^{-14}	0.6614	0.6140
14	1.60×10^{-13}	0.9067	0.7021	14	6.12×10^{-15}	0.5913	0.6195
15	1.15×10^{-13}	0.9168	0.7240	15	7.57×10^{-15}	0.6076	0.6478
16	8.28×10^{-14}	0.9183	0.6766	16	5.57×10^{-15}	0.4872	0.6707
17	5.96×10^{-14}	0.9220	0.7428	17	4.49×10^{-15}	0.6207	0.5773
18	1.18×10^{-13}	0.9539	0.6686	18	1.02×10^{-14}	0.7563	0.4890
19	1.23×10^{-13}	0.9077	0.7265	19	1.21×10^{-14}	0.7474	0.4867
20	8.75×10^{-14}	0.8675	0.8046	20	6.22×10^{-15}	0.6059	0.6122
21	1.08×10^{-13}	1.0248	0.6666	-	-	-	-
22	1.64×10^{-13}	0.9257	0.7127	-	-	-	-
Mean	1.11×10^{-13}	0.8265	0.7357	Mean	7.92×10^{-15}	0.06318	0.6068
Standard deviation	3.30×10^{-14}	0.1245	0.0602	Standard deviation	2.17×10^{-15}	0.0838	0.0595
CV (%)	1.13	15.07	8.18	CV (%)	0.85	13.27	9.80

246

247

248

Figure 7. Box-and-whisker plot of the material parameter involved in the moisture transfer simulation.

Grey box, PHS samples and white box, CHS samples. (a) ϕ , (b) $-\log(\alpha)$, (c) $-\log(K_{int})$, (d) m and (e) n

Figure 8 compares the intrinsic permeability values estimated in the WAC test (represented in Figure 7c) with those obtained in the contrast tests shown in Figure 4 (ASTM D5084 – 16 a). It can be observed that, as in the case of PHS, the coefficient of variation (CV) obtained in the estimation process is 1.13% (mean value $1.11 \times 10^{-13} \text{ m}^2$) as opposed to 0.55% (mean value $1.41 \times 10^{-13} \text{ m}^2$) obtained in the contrast tests. Similarly, in the case of the CHS, a CV of 0.85% was obtained (mean value $7.92 \times 10^{-15} \text{ m}^2$) in the estimated intrinsic permeability values, compared to 0.44 % (mean value of $8.45 \times 10^{-15} \text{ m}^2$) for the direct permeability tests. As seen, the range of variability is slightly higher in the parameters estimated for both lithotypes using the inverse analysis of WAC test. This increase in the CV may be because the WAC test is not designed to obtain a single material parameter. Even so, the CV reached via the estimation process is quite low (approximately 1%). Besides, the average values obtained with both strategies are almost identical. So, it appears that there is no reason to discard the representativeness of the parameters estimated from the proposed methodology.

Figure 8. Box-and-whisker plot of the negative logarithm of the intrinsic permeability obtained by (i) the hydraulic conductivity test (light grey on the left) and (ii) estimation process (dark grey on the right). (a) PHS and (b) CHS.

5.2 Stochastic sensitivity analysis

Given the inherent variability of the samples and the potential errors in the measurements taken in the WAC and the characterization tests, the estimated parameters have a certain variability. Figure 7 gives us an idea of their magnitudes, but it should be considered that they only approximately represent the marginal probability of each variable, without taking into account the correlations existing between the parameters. In ill-posed inverse problems, variables can be strongly correlated, resulting in disparate parameter combinations (some of which have no physical sense) leading to virtually identical behaviours being obtained when the direct problem is solved using the numerical tool [40].

To study the sensitivity of the model, the experimental marginal distributions of each parameter were analysed. It was assumed that the porosity (ϕ) and the parameters n and m of the van Genuchten water retention curve followed a normal distribution, taking a log-normal distribution for the intrinsic permeability (K_{int}) and the parameter α . The variance-covariance matrix associated with the set of vectors of estimated parameters was analysed for each lithotype, as well as the correlation between them, obtaining the results

shown in Table 3. Some important correlations between parameters can be observed, and thus, a sensitivity analysis of the model would be of interest.

A Monte Carlo-type stochastic study was conducted via random generation of parameter vectors $(\phi, -\log(\alpha), -\log(K_{\text{int}}), n, m)$ based on a multivariate normal function with the variance-covariance matrices shown in Table 3 that were calculated from the sample of estimated parameters shown in Table 2 and the corresponding values of ϕ and $-\log(\alpha)$ obtained from Eqs. (13) and (14). A total of 5000 random vectors were created for each lithotype. With this set of vectors, a set of direct simulations was created using the model described in the previous section in an intensive calculation effort, allowing the assessment of the sensitivity of the model to changes in the parameter values.

Table 3. Variance–Covariance and correlation matrix of estimated hygric parameters.

		Variance-Covariance matrix ($\times 10^{-4}$)					Correlation matrix				
		ϕ	$-\log(\alpha)$	$-\log(K_{\text{int}})$	n	m	ϕ	$-\log(\alpha)$	$-\log(K_{\text{int}})$	n	m
P H S	ϕ	6.714	8.984	-22.398	16.835	5.955	1.0000	0.2614	-0.5914	0.5217	0.3820
	$-\log(\alpha)$	8.984	175.957	24.244	102.472	-1.965	0.2614	1.0000	0.1250	0.6203	-0.0246
	$-\log(K_{\text{int}})$	-22.398	24.244	213.635	-59.806	-3.129	-0.5914	0.1250	1.0000	-0.3285	-0.0356
	n	16.835	102.472	-59.806	155.116	-28.871	0.5217	0.6203	-0.3285	1.0000	-0.3853
	m	5.955	-1.965	-3.129	-28.871	36.189	0.3820	-0.0246	-0.0356	-0.3853	1.0000
C H S	ϕ	4.218	24.399	-6.070	5.954	-0.399	1.0000	0.9929	-0.8451	0.8692	-0.4843
	$-\log(\alpha)$	24.399	428.381	-95.712	88.329	-3.792	0.9929	1.0000	-0.8046	0.8377	-0.4288
	$-\log(K_{\text{int}})$	-6.070	-95.712	144.971	-73.136	36.748	-0.8451	-0.8046	1.0000	-0.9655	0.8003
	n	5.954	88.329	-73.136	70.296	-42.296	0.8692	0.8377	-0.9655	1.0000	-0.8500
	m	-0.399	-3.792	36.748	-42.296	35.399	-0.4843	-0.4288	0.8003	-0.8500	1.0000

Figure 9 shows the ensemble of random simulations performed, along with the experimental data from the WAC tests of each lithotype. As seen, all tests performed on

both lithotypes are situated within the envelope defined by the simulations. PHS sample number 4 is found to be of special interest (corresponding with the outlier identified in the box-and-whisker plot of WAC coefficient, Figure 3), as it is situated in the lower boundary of the simulations band.

Figure 9. WAC tests simulations. Solid lines, simulation and marker with a dotted line, experimental data. (a) PHS and (b) CHS samples.

The results of Figure 9 were used to obtain the conditional probability density functions (PDF) of the water mass for an intermediate time ($t = 60$ s and $t = 300$ s for the PHS and CHS, respectively), using the kernel density estimator proposed by Botev [41]. They have been represented in Figure 10. For both lithotypes, it may be observed that all the experimental values are situated in the zone of 90% probability, with only that corresponding to test sample #4 of the PHS falling outside of this area. Likewise, 15 of the 22 tests of the PHS and 8 of the 20 CHS tests are situated in the 50% probability area.

Figure 10. PDF of water mass. Solid lines, simulations and marker, experimental data. (a) PHS, $t = 60s$ and (b) CHS, $t = 300s$.

Figures 10a and 10b allow for understanding the sensitivity of the model to changes in the parameters. In the case of having a very sensitive mathematical model to the parameter values, the stochastic simulation would have resulted in PDFs with higher variance and with simulations from the parameter set lacking physical sense. In the case of the PHS, the variability is greater for the CHS, while in both materials it may be seen that the probability distributions are asymmetric, with a greater tail in the area with the highest values, probably because some of the marginal distributions of the parameters are log-normal. In both cases, the PDFs are also unimodal, and the mean is not excessively separated from the mode, even though they are asymmetric PDFs. This gives confidence to the mathematical model used as well as on the estimated parameters. The mathematical expectation of the material behaviour coincides with the area of greatest probability and it is also the area where the greatest part of the experimental curves are located.

6. CONCLUSIONS

In this work, a methodology is presented that allows the estimation of the material parameters characterizing the moisture transfer process of the limestone used in the construction of the Cathedral of Santa María y San Julián in Cuenca (Spain), using

experimental data obtained through the commonly used water absorption by capillarity test (WAC test, EN 15801). The results offer the following conclusions:

- Based on the proposed methodology, it is possible to estimate the intrinsic permeability and the m and n parameters corresponding to the van Genuchten's model to determine the water retention curve. Similarly, with the information obtained from the WAC test, it is possible to calculate both the accessible porosity and the α parameter of the retention curve.

- The estimated parameters satisfactorily allow the modelling of the WAC test carried out on 42 samples of limestone.

- The quality of the proposed estimation method has been contrasted via the study of the dispersion obtained in the estimated values of intrinsic permeability, obtaining coefficients that were not greater than 1%, similar to those obtained in the direct determination of hydraulic conductivity tests. It is interesting to note that the variability of the estimated parameters is always less than that obtained in the determination of the WAC coefficient, indicating that the solution of the inverse problem offers precision according with the information included in the test.

- The statistical analysis of the estimated parameters and the sensitivity analysis of the model offers confidence to the estimation made, confirming that the hygric properties of both lithotypes have been consistently characterized and that the proposed mathematical model is appropriate.

Thus, it may be concluded that the proposed methodology is valid for the hygric characterization of selected limestone through an inexpensive and undemanding test such as the WAC test. At the same time, it can be considered as a viable alternative to

characterization techniques that include specific tests to estimate each material parameter individually using complex systems with high technical and economic costs.

Supplementary material

Supplementary material related to this work consists of information concerning (i) Mineralogical characterization of the limestone, (ii) numerical values of WAC coefficient, hydraulic conductivity determined experimentally, porosity, initial degree of saturation and α van Genuchten parameter.

Acknowledgements

The authors acknowledge funding support from (i) the Ministerio de Economía, Industria y Competitividad from Spanish Government and the European Union through the project [BIA2017-89287-R (AEI/FEDER, UE)], (ii) the Ministerio de Ciencia, Innovación y Universidades from Spanish Government through the Postdoctoral Grant [IJC-2018-035212] awarded to Dr López-Vizcaíno.

Symbol	Parameter
D_v	Binary diffusion coefficient of water vapour
g	Moisture flow rate
g_v	Water vapour flow rate
g_w	Liquid water flow rate
h	Piezometric head
k	Liquid conductivity
K	Hydraulic conductivity
K_{int}	Intrinsic permeability
K_{sat}	Saturated conductivity
m	Parameter of the van Genuchten's water retention curve
m_o	Mass of the sample at the start of the WAC test
m_{dry}	Dry mass of the sample
m_{sat}	Mass of the sample in saturated condition
MM_w	Molar mass of water
n	Parameter of the van Genuchten's water retention curve
P_G	Gas pressure
P_L	Liquid water pressure
P_v	Water vapour pressure
$P_{v, sat}$	Water vapour pressure at vapour saturated conditions
Q	Mass of water adsorbed per unit area
q	Water flow
R	Ideal gas constant
RH	Relative humidity
s	Suction
s_o	Suction at the begging of WAC test
Sr	Degree of saturation
Sr_o	Degree of saturation at the start of the WAC test
t	Time

Symbol	Parameter
T	Absolute temperature
$\hat{T}$	Temperature in Celsius degrees
V_T	Total volume
V_V	Void volume
V_W^{sat}	Water volume in saturated condition
w	Moisture content
w_o	Moisture content at the start of the WAC test
w_v	Water vapour content
w_w	Liquid water content
α	Parameter of van Genuchten's water retention curve
γ_w	Specific weight of the water
δ_0	Vapour permeability of still air
δ_p	Vapour permeability
κ	Relative permeability
μ	Diffusion resistance factor
μ_w	Dynamic viscosity of the liquid water
ρ_v	Water vapour density
$\rho_{v,\text{sat}}$	Water vapour density in saturated conditions
ρ_w	Liquid water density
τ_v	Tortuosity
ϕ	Porosity

373

374 **Appendix B. Water vapour density**

375 The density of water vapour, ρ_v , is obtained by the ideal gases law

$$376 \quad \rho_v = \frac{MM_w}{RT} P_v \quad (\text{B.1})$$

377 where R is the ideal gas constant [$\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$], T is the absolute temperature [K],

378 MM_w is the relative mass of water [kg mol^{-1}], and P_v is the water vapour pressure [Pa],

379 obtained from the psychrometric equation [42] as a function of suction, s

$$P = P_{v, \text{sat}} \exp\left(-\frac{MM_w s}{\rho_w RT}\right) \quad (\text{B.2})$$

where the vapour pressure in saturated conditions is given by

$$P_{v, \text{sat}} = \frac{RT}{MM_w} \rho_{v, \text{sat}} \quad (\text{B.3})$$

with $\rho_{v, \text{sat}}$ being the density of the water vapour in saturated conditions, calculated using the expression [31]

$$\rho_{v, \text{sat}} = \frac{\exp(0.06374\hat{T} - 0.1634 \cdot 10^{-3} \hat{T}^2)}{194.4} \quad (\text{B.4})$$

where $\hat{T}$ is the temperature [°C].

REFERENCES

- [1] UNESCO, Tourism Management at UNESCO World Heritage Sites, Università della Svizzera italiana, Lugano, 2018.
- [2] E. Franzoni, State-of-the-art on methods for reducing rising damp in masonry, *Journal of Cultural Heritage*, 31 (2018) S3-S9 <https://doi.org/10.1016/j.culher.2018.04.001>.
- [3] H. Künzle, A. Holm, Moisture Control and problem analysis of heritage constructions, PATORREB, 2009 (2009)
- [4] R. González, M. Varas-Muriel, M. Alvarez de Buergo, E. Pérez-Monserrat, Colmenar Limestone, Madrid, Spain: considerations for its nomination as a Global Heritage Stone Resource due to its long term durability, Geological Society, London, Special Publications, 407 (2014) 121-135 10.1144/SP407.8.
- [5] T. Vogel, J. Dusek, M. Dohnal, M. Snehota, Moisture regime of historical sandstone masonry — A numerical study, *Journal of Cultural Heritage*, 42 (2020) 99-107 <https://doi.org/10.1016/j.culher.2019.09.005>.
- [6] N. Karagiannis, M. Karoglou, A. Bakolas, A. Moropoulou, Building Materials Capillary Rise Coefficient: Concepts, Determination and Parameters Involved, *New Approaches to Building Pathology and Durability*, 6 (2016) 27-44 10.1007/978-981-10-0648-7_2.
- [7] M. Saba, J. Lizarazo-Marriaga, N.L. Hernandez-Romero, E.E. Quiñones-Bolaños, Physico-mechanical characterization of the limestone used in Cartagena walls and a proposal for their restoration process, *Construction and Building Materials*, 214 (2019) 420-429 <https://doi.org/10.1016/j.conbuildmat.2019.04.170>.
- [8] S.A. Orr, L. Fusade, M. Young, D. Stelfox, A. Leslie, J. Curran, H. Viles, Moisture monitoring of stone masonry: A comparison of microwave and radar on a granite wall and a sandstone tower, *Journal of Cultural Heritage*, 41 (2020) 61-73 <https://doi.org/10.1016/j.culher.2019.07.011>.
- [9] AENOR, UNE 41810:2017. Conservación del patrimonio cultural. Criterios de intervención en materiales pétreos., (2017)
- [10] CEN, EN 16515:2015. Conservation of cultural heritage - Guidelines to characterize natural stone used in cultural heritage, (2015)
- [11] D. Camuffo, Standardization activity in the evaluation of moisture content, *Journal of Cultural Heritage*, 31 (2018) S10-S14 <https://doi.org/10.1016/j.culher.2018.03.021>.
- [12] CEN, EN 15801:2009. Conservation of cultural property - Test methods - Determination of water absorption by capillarity, (2009)
- [13] CEN, EN 15803:2009. Conservation of cultural property - Test methods - Determination of water vapour permeability (delta [p]), (2009)

- 424 [14] CEN, EN 16322:2013. Conservation of cultural heritage - Test methods -
425 Determination of drying properties, (2013)
- 426 [15] J. Carmeliet, S. Roels, Determination of the isothermal moisture transport
427 properties of porous building materials, *Therm. Env. and Build. Sci.*, (2000)
- 428 [16] S. Galvan, C. Pla, N. Cueto, J. Martínez-Martínez, M.A. García-del-Cura, D.
429 Benavente, A comparison of experimental methods for measuring water permeability of
430 porous building rocks, *Materiales de Construcción*, 64 (2014) 10.3989/mc.2014.06213.
- 431 [17] N. Karagiannis, M. Karoglou, A. Bakolas, M. Krokida, A. Moropoulou, Drying
432 kinetics of building materials capillary moisture, *Construction and Building Materials*,
433 137 (2017) 441-449 10.1016/j.conbuildmat.2017.01.094.
- 434 [18] Z. Pavlík, P. Michálek, M. Pavlíková, I. Kopecká, I. Maxová, R. Černý, Water and
435 salt transport and storage properties of Mšené sandstone, *Construction and Building*
436 *Materials*, 22 (2008) 1736-1748 10.1016/j.conbuildmat.2007.05.010.
- 437 [19] E. Vejmelková, M. Keppert, P. Reiterman, R. Černý, Mechanical, hygric and
438 thermal properties of building stones, in: *WIT Transactions on the Built Environment*,
439 2013, pp. 357-367.
- 440 [20] T. Zurmühl, W. Durner, Determination of parameters for bimodal hydraulic
441 functions by inverse modeling, *Soil Science Society of America Journal*, 62 (1998) 874-
442 880 10.2136/sssaj1998.03615995006200040004x.
- 443 [21] C. Xu, S. Li, K. Zou, Study of heat and moisture transfer in internal and external
444 wall insulation configurations, *Journal of Building Engineering*, 24 (2019) 100724
445 <https://doi.org/10.1016/j.jobe.2019.02.016>.
- 446 [22] X. Shen, L. Li, W. Cui, Y. Feng, Coupled heat and moisture transfer in building
447 material with freezing and thawing process, *Journal of Building Engineering*, 20 (2018)
448 609-615 <https://doi.org/10.1016/j.jobe.2018.07.026>.
- 449 [23] W. Dong, Y. Chen, Y. Bao, A. Fang, A validation of dynamic hygrothermal model
450 with coupled heat and moisture transfer in porous building materials and envelopes,
451 *Journal of Building Engineering*, 32 (2020) 101484
452 <https://doi.org/10.1016/j.jobe.2020.101484>.
- 453 [24] E. Torrero, D. Sanz, V. Navarro, M. Arroyo, Non-destructive techniques used in
454 the chapel of Muñoz. Cathedral of Santa Maria of Cuenca, Spain. *Proceedings REHAB*
455 *2015, 2nd International Conference on Preservation. Maintenance and Rehabilitation of*
456 *Historical Buildings and Structures*, (2015) 821 - 832
- 457 [25] COMSOL, COMSOL Multiphysics Reference Manual Version: COMSOL 5.4.,
458 (2018)
- 459 [26] CEN, EN 15026:2007. Hygrothermal performance of building components and
460 building elements - Assessment of moisture transfer by numerical simulation, (2007)
- 461 [27] ASTM, ASTM D5084-16a. Standard Test Methods for Measurement of Hydraulic
462 Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter., (2016)

- [28] E. Torrero, Characterization, degradation and conservation of natural stones in the Cathedral of Santa María de Cuenca (in Spanish). PhD Thesis, University of Castilla-La Mancha, 2016.
- [29] CEN, EN 1936:2006. Natural stone test methods - Determination of real density and apparent density, and of total and open porosity, (2006)
- [30] V. Cabrera, R. López-Vizcaíno, Á. Yustres, M.Á. Ruiz, E. Torrero, V. Navarro, A functional structure for state functions of moisture transfer in heritage building elements, *Journal of Building Engineering*, 29 (2020) 101201 <https://doi.org/10.1016/j.jobbe.2020.101201>.
- [31] J. Ewen, H.R. Thomas, Heating unsaturated medium sand, *Geotechnique*, 39 (1989) 455-470 <https://doi.org/10.1680/geot.1989.39.3.455>.
- [32] M.T. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Science Society of America Journal*, 44 (1980) 892-898 <https://doi.org/10.2136/sssaj1980.03615995004400050002x>.
- [33] Y. Mualem, A new model for predicting the hydraulic conductivity of unsaturated porous media, *Water Resources Research*, 12 (1976) 513-522 <https://doi.org/10.1029/WR012i003p00513>.
- [34] S. Roels, Modelling unsaturated moisture transport in heterogeneous limestone, in: FACULTEIT TOEGEPASTE WETENSCHAPPEN, DEPARTEMENT BURGERLIJKE BOUWKUNDE, LABORATORIUM BOUWFYSICA, KATHOLIEKE UNIVERSITEIT LEUVEN, Leuven, 2000.
- [35] J. Carmeliet, S. Roels, Determination of the Moisture Capacity of Porous Building Materials, *Journal of Thermal Envelope and Building Science*, 25 (2002) 209-237 [10.1106/109719602022835](https://doi.org/10.1106/109719602022835).
- [36] R. Plagge, A. Teutsch, Water retention transfer functions of ceramic bricks of the Dresden building stock
- in: J. Carmeliet, H. Hens, G. Vermeir (Eds.) *Research in Building Physics - Proceedings of the Second International Conference on Building Physics*, Leuven, Belgium, 14-18 September 2003, Balkema, Lisse, The Netherlands, 2003, pp. 197-206.
- [37] D.W. Pollock, Simulation of fluid-flow and energy-transport processes associated with high-level radioactive-waste disposal in unsaturated alluvium., *Water Resources Research*, 22 (1986) 765-775 <https://doi.org/10.1029/WR022i005p00765>.
- [38] J.R. Philip, D.A. De Vries, Moisture movement in porous materials under temperature gradients, *Eos, Transactions American Geophysical Union*, 38 (1957) 222-232 <https://doi.org/10.1029/TR038i002p00222>.
- [39] J.A. Nelder, R. Mead, A simplex method for function minimization, *Computer journal*, 7 (1965) 308-313
- [40] J. Carrera, A. Alcolea, A. Medina, J. Hidalgo, L.J. Slooten, Inverse problem in hydrogeology, *Hydrogeology Journal*, 13 (2005) 206-222

- 502 [41] Z.I. Botev, J.F. Grotowski, D.P. Kroese, Kernel density estimation via diffusion,
503 Annals of Statistics, (2010)
- 504 [42] N. Edlefsen, A. Anderson, Thermodynamics of soil moisture, Hilgardia 15 (1943)
505 31-298 <https://doi.org/10.3733/hilg.v15n02p031>.
- 506