Pergamon

Cement and Concrete Research 32 (2002) 1883–1888

CEMENT AND CONCRETE RESEARCH

Pore structure in mortars applied on restoration Effect on properties relevant to decay of granite buildings

M.J. Mosquera[a,*], D. Benítez[a], S.H. Perry[b,✠]

[a]Departamento de Química-Física, Facultad de Ciencias, Universidad de Cádiz, P.O. Box 40, Puerto Real, Cádiz, 11510, Spain
[b]Department of Civil, Structural and Environmental Engineering, Trinity College, Dublin 2, Ireland

Received 5 February 2002; accepted 28 May 2002

Abstract

Since mortars play a key role in buildings decay, their suitable choice is critical to the success of restoration projects. The focus of this paper is to characterise the pore structures of a set of mortars and correlate them with mechanical properties and vapour permeability, which are relevant to the decay of granite buildings. Water vapour transport was tested by means of a simple set-up developed in our laboratory. A good correlation was found between total porosity and the two parameters tested: strength and vapour diffusivity. Pore size distribution also showed a strong influence on diffusivity. A mix based on cement with a high sand proportion was considered as the most suitable for granite building restoration because it showed good mechanical properties and low free calcium content. A negative aspect was that this mix exhibited significantly lower vapour permeability than mortar containing lime; this could be explained by the smaller radius of its pores.

Keywords: Mortar; Mechanical properties; Transport properties; Microstructure; Restoration

1. Introduction

Granite is considered as a highly durable building stone compared to calcareous rocks. However, granite decay has been observed in numerous buildings. As has been widely reported [1,2], soluble salt crystallisation in the porous structure of stone is one of the most important reasons for decay. In fact, the crystallization of a mineral phase from ions in solution may develop significant local pressures, which are even higher than the tensile strength of the stone [3]. Moreover, volumetric expansion of salts induced by the growth of hydration crystals, or by temperature increases, may also cause stress [4]. These forces lead to the formation of cracks in granites. On the other hand, the presence of salts in rock pores may cause the dissolution of quartz, which is a main component of the rock [5]. In severe instances, disruption and disintegration of the entire stone surface can be observed.

Since pointing mortars constitute a large percentage of the surface of many buildings, for several reasons, they play a key role in building decay [6]. Firstly, as mortars are in direct contact with both surface environment and the surrounding stone, decay products from mortars are deposited directly onto the stone, causing damage. In fact, the lime mortars commonly used in buildings until well into the 19th century represent a potential source of damage ions, especially calcium. The free calcium dissolves in water present in the stone and then reacts with sulphates from the environment to form mainly gypsum, which is the most common and most damaging form of hydrated calcium sulphate. A previous study [7] revealed a clear correlation between building areas of damaged granite and sources of calcium, such as lime mortars. Secondly, mortars show a great influence in moisture transport on buildings, which is a key factor in salt-induced decay. Mortars that are more permeable to water vapour than granite significantly reduce the transport of damaging ions in the pore structure because water evaporates quickly through the mortar pores. Finally, the mechanical properties of mortars play a significant role in the event of even a slight movement of the wall. Strong pointing mortars restrain movements of stone units rather than accommodate them. It leads to stress build-up in the wall, which can cause severe rupture of stones. Thus, a repointing mortar should be considerably weaker than the stone and deform significantly before failure.

* Corresponding author. Tel.: +34-956-016-331; fax: +34-956-016-288.
E-mail address: mariajesus.mosquera@uca.es (M.J. Mosquera).
✠ 1940–2002 deceased.

0008-8846/02/$ – see front matter
PII: S0008-8846(02)00887-6

Therefore, the choice of repointing mortars in restoration projects is a key decision in order to avoid subsequent stone decay. The replacement by cement of traditional lime as binder permits reduction of the free calcium content. However, it is well known [8] that the use of mortars based on cement can cause severe damage in buildings due to cement being too hard, rigid and impermeable. In order to solve these disadvantages, Duffy et al. [6] developed a new cement mortar containing a high aggregate/binder ratio (9:1) compared to typical mortars. This mix, which had low free calcium content, showed mechanical properties suitable for buildings repointing.

The purpose of this paper is to evaluate the effect of the pore structure of mortars on properties specific to granite decay. In order to establish relationships with the microstructure, the mechanical and transport properties of a set mortar are obtained experimentally. As no commercial instrument was available for the automatic measurement of water vapour transport measurement, the necessary set-up has been developed in our laboratory. Free calcium content, which is the other factor inducing decay, is also evaluated. The relevance of this study stems from the possibility of using textural properties for optimising mortars used in restoration projects.

2. Experimental work

2.1. Mortars

Typical cement and lime/cement mortars, which are widely used in building construction, were compared with two cement mixes with high aggregate/binder ratio. An admixture, which improved mix workability, was included in the last two mortars. Additionally, a mortar in which the binder was partially replaced by pulverised clay brick as a pozzolanic material was tested. It permitted an investigation into the potential of recycling waste brick in the manufacture of mortars. Finally, a commercially available product, Euromix (CPI, Dublin, Ireland), was also evaluated. Details of mix proportions are given in Table 1. Mortars were prepared in accordance with BS 4551 (1980) [9] as 0.1-m cubes. All mixes consisted of sand with 2 mm maximum aggregate size and ordinary Portland cement (OPC). A particle size for the ground brick similar to that of cement was obtained for by plate grinding and then ball milling. A water/binder ratio ranging from 0.6 to 0.8 gave a suitable workability for all mixes. Mortars were maintained in the moulds for 24 h and were then cured under damp conditions for 28 days. All results reported were an average value of three similar specimens. The coefficients of variation were below 10%.

Table 1
Mortars composition

Mix	Materials	Ratio (by weight)
1	Sand/cement	3:1
2	Sand/cement/admixture[a]	6:1
3	Sand/cement/admixture[a]	9:1
4	Sand/lime/cement	6:1:1
5	Sand/pozzolan/cement	6:1:1
6	Euromix® (sand/cement/admixtures)	6:1[b]

[a] WRDA® 27 (Grace Canada) was included. Dosage was 240 ml/100 kg of cement.

[b] According to manufacturer's specifications.

2.2. Pore structure

Textural properties were characterized by Mercury Intrusion Porosimetry (MIP). The measurements were carried out using a Pascal Porosimeter (Fisions Instruments Milan, Italy) over the pressure range between 10^{-3} and 400 MPa. Specimens, with an average volume of 2 cm^3, were cut from mortar cubes by low-speed sawing. Before testing, specimens were cleaned in a microwave bath and were dried at 60 °C until constant weight was achieved.

2.3. Mechanical properties

Compression strength tests were conducted on the mortar cubes using a Denison compression machine at low rates of loading (5 kN/min). Vertical strain was monitored using electrical resistance strain gauges (10 mm in length).

2.4. Vapour transport

Water vapour transport was investigated by means of an automatic set-up developed in our laboratory. The device, which is based on the standard cup test [10–12], is a modification of an earlier moisture absorption-measuring apparatus [13]. A schematic diagram of the experimental set-up is shown in Fig. 1. The following components were included: the scale of a suspended weighing device (A) interfaced with a computer (B) and a climatic chamber (C), which is located below (A). The chamber consists of a gas-tight methacrylate receptacle ($275 \times 185 \times 247$ mm) wherein stable moisture and temperature are achieved. An environment sensor (D) is also interfaced with the computer. A specimen support cup (E), which is a methacrylate cube (52 mm) without an upper side, is placed into the climatic chamber. A wire attached to the scale holds the cup.

The test procedure was as follows. Specimens were cut from mortar cubes as slabs of 40 mm side and 10 mm thickness. After samples were dried at 60 °C until constant weight, they were placed as a cover over the cup. A moisture saturated ambient condition (RH 98%) was maintained in the cup. The specimen cup perimeters were sealed with silicone paste A (Panreac Química S.A., Barcelona, Spain). The climatic chamber was maintained at laboratory temperature (17 °C) during all the experiments. At the start of tests, low relative moisture (3%) was achieved in the chamber by means of a desiccating agent (Silicagel; Panreac Química S.A., Barcelona, Spain). In these conditions, the

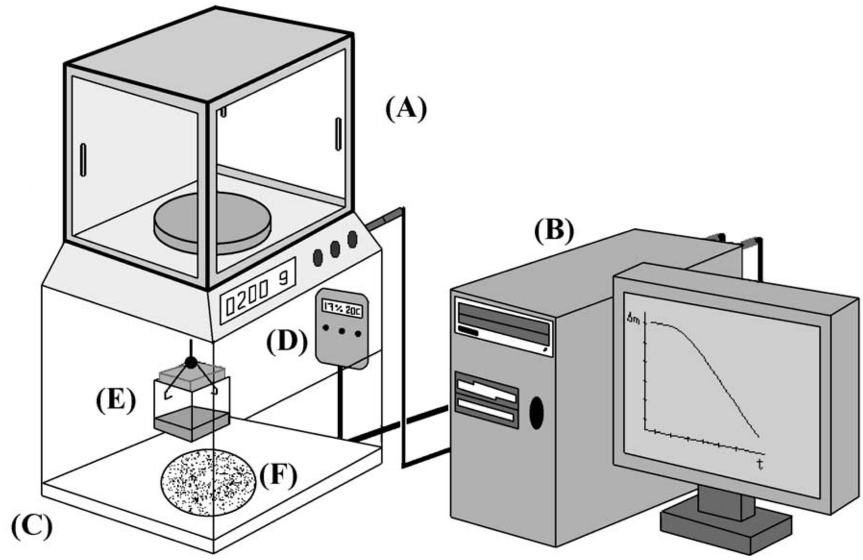

Fig. 1. Schematic of experimental set-up for water vapour transport measurements. (A) scale; (B) computer; (C) climatic chamber; (D) environmental sensor; (E) specimen support cup; (F) silica gel.

moisture gradient across the specimen promoted water vapour flux. The monitoring of the cup mass decrease permitted the progress of vapour transport to be determined. It was registered continuously and displayed in situ by use of the computer software. Moreover, the computer registered temperature and relative moisture in the chamber during tests. As would be expected, after an initial increase of moisture into the climatic chamber, for all tests, moisture was stabilized at around an RH of 20%.

2.5. Free calcium

Total soluble calcium content analyses were carried out on cores drilled from the mortar cubes. Five grams of powder of each specimen was eluted in 100 ml of deionised water. For the filtered solutions, Ca^{+2} concentration was determined by atomic absorption. A Perkin-Elmer 3100 atomic absorption spectrophotometer was used (Perkin-Elmer, Grace Canada, Ontario, Canada).

3. Results and discussion

3.1. Pore structure

Results of MIP tests in terms of total porosity are given in Table 2, while pore radius distributions are shown in Fig. 2. Differential volumes of mercury in specific ranges, which are shown in a logarithmic distribution, are plotted against medium pore radii. For mortars containing exclusively cement as binder, it was observed that cement reduction increased the total porosity. Addition of lime or a pozzolan increased comparative porosity because mixes containing these binders exhibited a significantly higher porosity than that of cement mortar with similar sand/binder ratio (6:1). The commercial product showed a high porosity, which could be related to unknown additives incorporated by the manufacturer.

In relation to pore size distribution (Fig. 2), the mortars based on cement, including the commercial product, had a very similar distribution. The porous volume was in the pore range of 100–2 nm. The maximum volume intruded corresponded to a radius of about 9 nm. The presence of other binders in the mixes had influence on the distribution. In fact, the addition of lime significantly increased the threshold radius. Lime/cement mortar showed a wider distribution with a shift of larger pores in the pore range of 400–100 nm. The threshold radius of pozzolan mortar was similar to that of cement mortars, but its maximum exhibited a clear bidispersion at about 20 and 4 nm.

3.2. Mechanical properties

Compressive strength results are illustrated in Table 2. The cement mortar with the lowest sand proportion (3:1) gave the highest strength, followed by the commercial product. For

Table 2
Mortars' properties

Mix	Porosity (%)	Strength (N/mm^2)	Modulus 10^{-3} (N/mm^2)	Diffusivity 10^{-6} (m^2/s)	Ca^{2+} (mg/l)/g sample[a]
Sand/cement 3:1	16.68	37.0	20.0	0.85	55.5
Sand/cement 6:1	18.34	9.5	8.1	1.58	41.5
Sand/cement 9:1	24.60	5.2	2.4	2.53	26.0
Sand/lime/cement	24.21	6.2	1.6	7.54	77.0
Sand/pozzolan/cement	22.70	6.5	4816.0	1.89	50.5
Euromix®	32.84	23.0	12.0	3.27	98.0

[a] This means milligram of soluble calcium extracted from 1 l of deionised water per gram of sample.

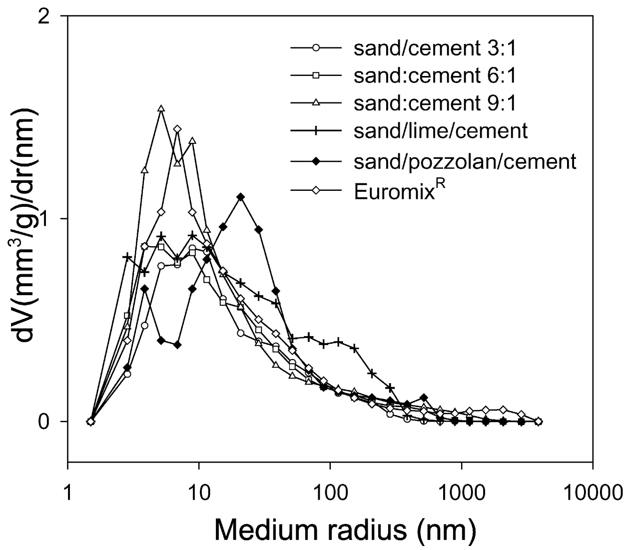

Fig. 2. Pore radius distributions.

cement mortars, sand increase in the mix reduced significantly their strength. Mortars, including lime and pozzolan, exhibited similar values, which were lower than that of the cement mortar with a similar sand/binder ratio (6:1). The strength reduction could be related to its higher porosity. The commercial product strength was unusually high given its high sand/cement ratio. Clearly, this must be associated with the effects of the admixtures incorporated by the manufacturer.

Fig. 3 shows stress–strain curves and Table 2 gives moduli of elasticity. Mortar moduli showed the same trend as the strength values and, thus, a clear connection between both parameters was observed. Cement mortar (3:1) and the commercial product, with the highest strengths, exhibited the highest moduli. However, the pozzolanic mortar showed an anomalous behaviour because its elastic modulus was exceptionally high, while its strength was low. As observed in Fig. 3, strain at failure was significantly greater for the lime/cement mix. Only the cement mortar with the highest sand/cement ratio (9:1) and porosity, close to a lime mortar, reached a similar strain.

3.3. Vapour transport

Permeation curves corresponding to steady-state flow are showed in Fig. 4. Since each curve contains a high number of data points, only the line joining these points is shown. Assuming that Fick's law describes the flow of water molecules towards the lower vapour pressure, diffusion coefficients were obtained from the equation:

$$Q = D\frac{A\Delta C}{l}t \qquad (1)$$

where D is vapour diffusivity (m^2/s); Q is cup mass decrease (g); l is specimen thickness (m); A is specimen area (m^2), ΔC is moisture concentration gradient (g/m^3) and t is time (s).

Therefore, by plotting Ql/Ah versus the time (Fig. 4), vapour diffusivity values, which are shown in Table 2, were calculated directly from the slope of a linear regression of data. High regression coefficients (r>.99) were obtained for all plots. As described in the Experimental Work section, a steady vapour flow was reached when the relative moisture in the climatic chamber was stabilized. This occurred in a time range between 5 and 18 h. Tests were finished when a minimum of 2000 experimental data readings was obtained (around 30 h). This high number of readings permitted an exact characterization of the transport process. The low standard deviations obtained between replicates indicated

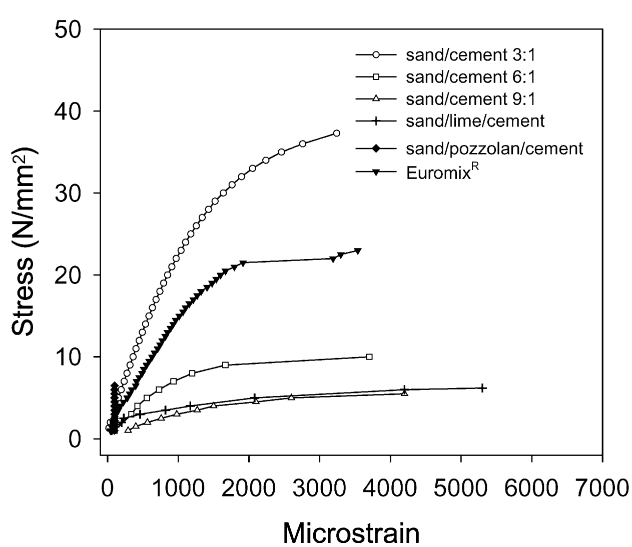

Fig. 3. Stress–strain curves. Strain is defined as fractional change in length of the material due to the applied stress. Therefore, it is dimensionless. Microstrain is $10^{-6} \times$ strain.

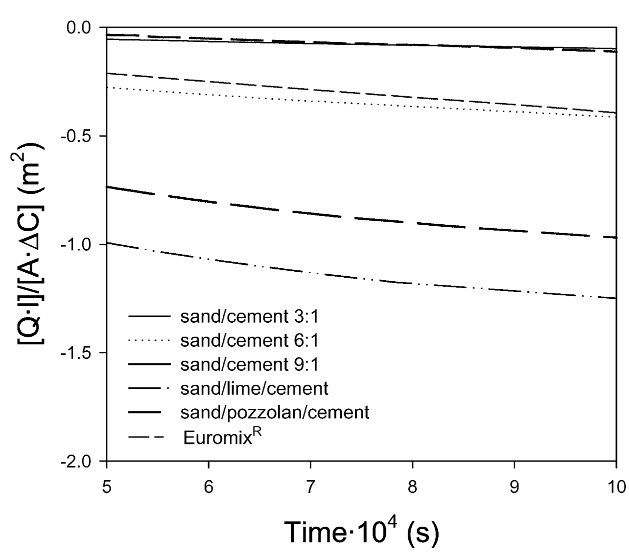

Fig. 4. Vapour diffusivity curves. Q is cup mass decrease (g); l is specimen thickness (m); A is specimen area (m^2); and ΔC is moisture concentration gradient (g/m^3).

the good reproducibility of the experimental set-up. By contrast, existing standard tests are manual procedures where the low number of readings obtained has made for poor discrimination in material changes [14].

As it is showed in Table 2, vapour diffusivity values were found to increase with the sand proportion in the cement-based mixes, including the commercial product. Addition of other binders caused deviations of this behavior, which were comparatively large in the lime mortar. Diffusivity of this mortar was found to be exceptionally high.

3.4. Free calcium

Results for soluble calcium content are shown in Table 2. As was expected, lime/cement mortar was higher in free calcium than cement mortars. For these mixes, calcium content was found to reduce with increase in sand/binder ratio. Pozzolan/cement mortar was of comparable calcium content to cement mortars, indicating that the pozzolan did not modify significantly the free calcium quantity in the mix. The commercial product showed the greatest value.

3.5. Effect of pore structure on mechanical properties

It is well known that pore structure plays an important role on the strength of cement-based materials. Many experimental results have confirmed that an acceptable prediction of strength can be obtained by using total porosity [15]. In Fig. 5, strength values are plotted versus total porosity. As a general trend, strength was found to reduce with increasing in porosity. The commercial product showed an anomalous behaviour that could be explained by the effect of admixtures. In relation to mixes prepared in the laboratory, a linear relationship (r=.98) between strength and porosity was exhibited except for the sand/cement 3:1 mix, where a much higher strength emerged, compared to porosity. Addition of admixtures and other binders could explain the abrupt reduction of strength.

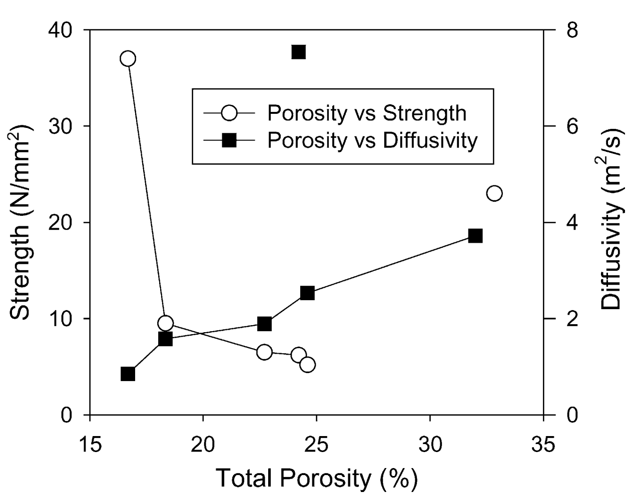

Fig. 5. Relationship among strength, vapour diffusivity and mortar porosity.

3.6. Effect of pore structure on vapour transport

Many models and theories have been proposed to correlate water permeability and pore structure of cementitious materials [16–18], it being generally accepted that a combination of porosity and pore size represents the most suitable parameter for expressing this relation. Curves of total porosity versus vapour diffusivity are plotted in Fig. 5. A good linear correlation (r=.98) was observed except for the data from the lime/cement mortar. This was explained by the closed pore distribution of mixes. In fact, as it is seen in Fig. 2, mortars based on cement showed similar distributions, with identical maximum values of pore volume. In the case of mortars containing pozzolan, the correlation was maintained with both the distribution range as well as the average value between the two maximum values being similar. The high diffusivity value for the lime mortar corroborated the pore size effect on transport properties. This could be explained by the difference in its pore distribution. As can be appreciated from Fig. 2, this mix showed a porous volume ranging from 100 to 400 nm, much greater than that observed in other mixes.

4. Conclusions

The following conclusions were drawn.

(1) The total porosity of mortars was modified by the sand/binder ratio in the mix. Binder composition had a significant influence on pore size distribution.

(2) The simple experimental set-up developed in our laboratory allowed detailed investigation of water vapour transport in the mortars tested and provided an acceptable repeatability of results.

(3) A good correlation between total porosity and strength was observed. Where they existed, deviations from this general trend were attributed to the effects of admixtures and different binders.

(4) A good correlation between total porosity and vapour diffusivity was established for mortars with closed pore distribution. The anomalous trend shown by the lime/cement mortar was explained by differences in its pore distribution.

(5) Among all mortars tested, the 9:1 sand/cement mix was found to be the most suitable for the repointing of granite buildings. This was because it showed suitable mechanical properties, similar to those for the lime/cement mix, and had the lowest free calcium content. As a negative aspect, this mix exhibited significantly lower vapour permeability than mortar containing lime. This could be explained by the smaller radius of the pores.

(6) From (5), it is possible to conclude that the pore structure of mortars has permitted the modelling of properties relevant to the decay of granite buildings. Further work in progress is focused on increasing vapour permeability of cement mortar by the addition of admixtures to increase the pore radius.

Acknowledgements

Part of the experimental work was developed during a postdoctoral stay of Dr. M.J. Mosquera in Trinity College, Dublin. The authors would like to thank Dr. A.P. Duffy, Dr. R.P. West and technicians from the Civil Engineering Department at Trinity College for support in the experimental work. Thanks are also due to Dr. J. Martín from University of Cádiz for an essential contribution to the development of the test set-up for measuring vapour diffusivity.

References

[1] G. Amoroso, V. Fassina, Stone decay and conservation: Atmospheric pollution, cleaning, consolidation and protection, Materials Science Monographs, vol. 11, Elsevier, Amsterdam, 1983 (453 pp.).

[2] S.H. Perry, A.P. Duffy, The short-term effects of mortar joints on salt movement in stone, Atmos. Environ. 31 (9) (1997) 1297–1305.

[3] D. Benavente, M.A. García del Cura, R. Fort, S. Ordóñez, Thermodynamic modelling of changes induced by salt pressure crystallisation in porous media of stone, J. Cryst. Growth 204 (1999) 168–178.

[4] R. Rossi-Manaresi, A. Tucci, Pore structure and the disruptive or cementing effect of salt crystallization in various types of stone, Stud. Conserv. 36 (1991) 56–58.

[5] A.R.M. Young, Salts as an agent in the development of cavernous weathering, Geology 15 (1987) 962–966.

[6] A.P. Duffy, T.P. Cooper, S.H. Perry, Repointing mortars for conservation of a historic stone building in Trinity College, Dublin, Mater. Struct. 26 (1993) 302–306.

[7] P.F. O'Brien, E. Bell, S. Pavia Santamaria, P. Boyland, T.P. Cooper, Role of mortars in the decay of granite, Sci. Total Environ. 167 (1995) 103–110.

[8] K. Callebaut, J. Elsen, K. Van Balen, W. Viaene, Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium). Natural hydraulic lime or cement? Cem. Concr. Res. 31 (2001) 397–403.

[9] British Standard BS 4551, Methods of Testing Mortars, Screeds and Plasters (Laboratory Preparation of Mortar Mixes), British Standard Institution, London, 1998, pp. 14–17.

[10] Instituto Centrale do Restauro-Commisione Normal (ICR-CNR), Doc. Normal 21/85. Alterazioni dei materiali Lapidei e Trattamenti Conservativi. Proposte per L'Unificazione dei Metodi Sperimentali di Studio e di Controlo. Permeabilita al vapor d'acqua, Rome, Italy, 1985.

[11] American Society of Testing Materials, ASTM E96-90. Standard Test Methods for Water Vapor Transmission of Materials, ASTM, Philadelphia, PA, 1990, pp. 685–695.

[12] Deutsches Institut fuer Normung, DIN 52615. Bestimmung der Wasserdampf-durchlässigkeit von Bau-und Dämmstoffen, BEUTH, Berlin, 1987.

[13] M.J. Mosquera, R. Alcántara, J. Martín, A new procedure for performance moisture absorption tests, Am. Ceram. Soc. Bull. 77 (9) (1998) 76–81.

[14] T. Rivas, B. Prieto, B. Silva, Permeability to water vapour in granitic rocks. Application to the study of deleterious effects of conservation treatments, Build. Environ. 36 (2001) 239–246.

[15] C. Shi, Strength, pore structure and permeability of alkali-activated slag mortars, Cem. Concr. Res. 26 (12) (1996) 1789–1799.

[16] L. Bágel, V. Cívica, Relationship between pore structure and permeability of hardened cement mortars: on the choice of effective pore structure parameter, Cem. Concr. Res. 27 (8) (1997) 1225–1235.

[17] H.W. Reinhardt, K. Gaber, From pore size distribution to an equivalent pore size of cement mortar, Mater. Struct. 23 (1990) 3–15.

[18] A.S. El Dieb, R.D. Hooton, Evaluation of the Katz–Thomson model for estimating the water permeability of cement based materials from Mercury Intrusion Porosimetry data, Cem. Concr. Res. 24 (3) (1994) 443–455.