Available online at www.sciencedirect.com





Journal of the European Ceramic Society 24 (2004) 547-564

www.elsevier.com/locate/jeurceramsoc

Influence of mineralogy and firing temperature on the porosity of bricks

Giuseppe Cultrone^{a,*}, Eduardo Sebastián^a, Kerstin Elert^a, Maria José de la Torre^b, Olga Cazalla^a, Carlos Rodriguez–Navarro^a

> ^aDepartamento de Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n 18002 Granada, Spain ^bDepartamento de Geología, Universidad de Jaén, c/Alfonso X El Sabio 28, 23700 Linares, Jaén, Spain

> > Received 2 November 2002; accepted 6 March 2003

Abstract

The changes in brick porosity upon firing (700 up to 1100 °C) and its relation to the mineralogical composition are examined. Two types of raw clay with a composition representative of that used in brick-making industry were selected to manufacture the bricks: one contains notable amounts of carbonates, with a grain size of under 1 mm, and the other is predominantly quartzitic and lacking in carbonates. We demonstrate that the presence or absence of carbonates strongly influences the porosity development and, therefore, the brick texture and physical-mechanical properties. The carbonates in the raw clay promote the formation of fissures and of pores under 1 µm in size when the bricks are fired between 800 and 1000 °C. The absence of carbonates results in a continuous reduction in porosity and a significant increase in the pore fraction with a radius $(r) > 1 \mu m$ as the firing temperature rises and smaller pores coalesce. Porosity and pore size distribution results obtained from the combined use of hydric tests (HT), mercury intrusion porosimetry (MIP) and digital image analysis (DIA) of scanning electron microscopy photomicrographs are compared. A clear correlation between the water absorption and drying behaviour of the bricks and the porosity plus pore size distribution is observed. DIA discloses the evolution of size, shape and connectivity of macropores ($r > 1 \mu m$) and evidences that MIP results underestimate the macropore content. Conversely, MIP gives a good estimate of the open porosity and of the distribution of pores with $r < 1 \mu m$. It is concluded that the combined use of these complementary techniques helps to fully characterise the pore system of bricks. These results as well as the study of the evolution of the speed of ultrasound waves vs. time yield useful information to evaluate the bricks physical-mechanical behaviour and durability. The relevance of these findings in the conservation of historic buildings is discussed. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Bricks; Clays; Electron microscopy; Microstructure-final; Porosity

1. Introduction

Rocks and many artificial construction materials (e.g., bricks, mortar, concrete, etc.) are composed of monoor polymineral aggregate and empty spaces. These empty spaces (pores and fissures) are an essential component of the material since their volume, size and distribution affect its characteristics for industrial use and weathering behaviour, when used for structural or ornamental purposes.¹

The pore volume and pore size determine the capacity for fluid storage and the ease of fluid circulation within the materials, both inevitably favouring their deterioration.^{2,3} Moreover, variations in the porosity markedly affect the mechanical resistance of building materials.⁴ The porosity and, particularly, the pore-size distribution (PSD) have been considered as key parameters for predicting the durability of different building materials, and especially bricks, subjected to various types of weathering phenomena in aggressive environments (e.g., acid rain-related attack and dissolution, salt crystallisation and freeze-thaw cycles).^{2,5-7} It has been experimentally demonstrated that bricks (as well as other construction materials such as stone or mortar) with a high porosity and a high percentage of pores with $r < 2.5-1 \mu m$ are most susceptible to weathering, particularly due to salt crystallisation and freeze-thaw phenomena.^{2,5,6,8,9} Thus, porosity and PSD have been considered crucial parameters to determine the durability of construction

^{*} Corresponding author. Tel.: +34-958-248335; fax: +34-958-243368.

E-mail address: cultrone@ugr.es (G. Cultrone).

^{0955-2219/03/\$ -} see front matter 0 2003 Elsevier Ltd. All rights reserved. doi:10.1016/S0955-2219(03)00249-8

materials.¹⁰ However, durability indexes for bricks based solely on total porosity and PSD determined by means of MIP^{5,6} are questioned due to this technique important limitations.¹¹

Firing of clay bricks produces a series of mineralogical, textural, and physical changes that depend on many factors and influence porosity. As an example, grain size is a significant parameter, since ceramics manufactured with a high sand fraction tend to be very porous and permeable.¹² Significant variations in the composition and/or concentration of mineral phases also cause changes in the pore system.¹³ It has been shown, for instance, that a high proportion of calcite produces more porous ceramics due to its high temperature (T) decomposition and the release of CO_2 .¹⁴ The physical-chemical changes that occur during firing are partly responsible for volume changes in ceramics. These changes comprise rapid, uneven expansion and contraction associated with chemical-structural changes that can show up as exothermic or endothermic reactions.¹⁵ Generally, products fired at high T are more vitreous and undergo the greatest changes in size (contraction) and porosity.^{10,16-18} Contraction and, therefore, an excessive reduction in porosity during the firing of a raw clay, can be reduced by mixing it with brick dust obtained by firing the same clay. The added brick dust does not cause changes in the mineralogical composition, and its volume is not reduced during the second firing.¹⁹ On the other hand, the porosity can be increased without altering the composition by adding to the clay a material that will calcinate completely, for example, coal powder.¹⁴

Although the water absorption behaviour, density and porosity of different types of bricks have been studied and compared,^{5,10,20} there is still no detailed explanation of their relationship with the textural features of the ceramics after firing. Some relationships between clay mineralogy and porosity are known,^{21,22} but the effects of the presence of new mineral phases on the porosity and its possible evolution over time have not been well established. On the other hand, the study of the pore system of ceramics is normally performed using a single technique (e.g., mercury intrusion porosimetry, MIP).11 The instrumental limitations and imprecision of most common techniques for porosimetry analysis lead to incomplete, sometimes misleading results if used alone.²³ The joint application of complementary analytical techniques based both on the direct observation of the pore system (i.e. optical and electron microscopy coupled with digital image analysis, DIA)²⁴⁻²⁶ and on the indirect evaluation of the porosity and PSD (e.g., MIP and hydric tests, HT)^{2,6,18,27} to characterise the pore system of ceramics may help solve this problem. Since the information on porosity strongly depends on the experimental technique employed,²⁸ the combined use of the above mentioned techniques may

yield both important information regarding limitations of a particular technique and a more accurate/complete picture of the pore system of bricks. Nonetheless, to our knowledge there is no study of the pore system of bricks performed combining the use of all of the above mentioned techniques (i.e. HT, DIA and MIP).

The accurate and thorough study of the bricks pore system is important not only to further our knowledge of ceramics, but also due to the interest in civil engineering and architecture regarding the physical–mechanical characteristics of these building materials. These characteristics include the reduction in both the mechanical resistance over time because of fluid circulation in the pore system of solid bricks,²⁹ and the bonding strength between the bricks and mortars or cements and other building materials.³⁰

The main aim of this work is to shed light on the relationships among the raw clay composition, firing temperature, porosity and PSD of solid bricks, through the analysis of results obtained using different analytical techniques. Knowing these relationships will aid in evaluating the physical-mechanical performance and the durability of bricks and their compatibility with other building materials. Thus this study may have important implications in the conservation of historic structures made of bricks.

2. Materials and methods

The solid bricks were prepared by hand in the laboratory. Water was added (400 ml/kg raw material) to make the clay plastic. The clay was then placed in a wooden mould to shape the bricks, which were subsequently air-dried. The average T and relative humidity (RH) in the laboratory were 25 °C and 50%, respectively. Two types of clays were used: one (V) contains significant amounts of carbonates: calcite and dolomite with a micritic and sparitic texture. Grain size varied, but was never over 1 mm. The other clay (G) is predominantly siliceous and lacking in carbonates. It has a higher concentration of phyllosilicates (i.e. clay minerals). Details on raw clay mineralogical composition and grain size distribution have been published elsewhere.³¹

These two clays are considered representative of the main types of raw clay materials commonly used in brick-making industry.^{32,33} The use of carbonates in ceramic products was already common in Roman times when lime-rich marls were chosen in the production of "terra sigillata".³⁴

The samples were fired in an electric oven (Herotec CR-35) at T of: 700 °C (G7 and V7), 800 °C (G8 and V8), 900 °C (G9 and V9), 1000 °C (G10 and V10) and 1100 °C (G11 and V11). The temperature was increased by increments of 3 °C per min, and was maintained

constant for 1 h at 100 °C and 3 h at the maximum T for that run.

The mineralogy was determined by X-ray diffraction (XRD), using a Philips PW 1710 diffractometer equipped with an automatic slit window. The settings were: CuK_{α} ($\lambda = 1.5405$ Å), 3 to 60°2 θ explored area and goniometer speed of 0.01 °2 θ /s. Semiquantitative analysis of mineral phases was performed using experimentally determined reflectance power of each phase, according to the methods proposed by Culliti³⁵ and Rodríguez Gallego.³⁶

The textural evolution of the bricks and the changes in the components of the prograde phases were studied by scanning electron microscopy (SEM), using a Zeiss DMS 950 SEM coupled to an EDX Link QX 2000 microanalyser. Details of phase transformations (i.e. dehydroxilation and partial melting of phyllosilicates, as well as high-T aluminosilicate phases formation) were observed using a transmission electron microscope (Philips CM20), operated at a 200 kV acceleration voltage and equipped with an EDAX solid-state energydispersive X-ray detector with an ultra-thin window (UTW). The objective aperture was 40 μ m, which is a compromise between amplitude and phase contrast images. Prior to TEM observations, the selected areas of a Canadian balsam-mounted thin section were removed, further thinned using a Gatan 600 ion-mill and finally carbon-coated (as in Barber).³⁷

The parameters associated to fluid uptake and transport inside the pores were determined by hydric tests immediately after removing the bricks from the kiln and cooling them to about 25 °C. Water absorption,³⁸ drying³⁹ and capillary uptake⁴⁰ were determined by weighing the samples (three samples per brick type) at regular intervals. The absorption coefficient, the drying rate,³⁹ the apparent density, and the open porosity were calculated. The samples used for water absorption and drying tests were cubic (3 cm per side), whereas the ones for the capillarity test were parallelepiped (7×3.5×2 cm).

The distribution of the pore access size and its evolution as a function of the firing T, as well as the pore volume, were determined by mercury intrusion porosimetry (MIP). Freshly cut brick chips of ca. 2 cm^3 were oven dried for 24 h at 110 °C and subsequently analysed using a Micromeritics AutoPore III 9410 porosimeter. Two MIP measurements per brick were made. SEM secondary electron images of polished thin sections of brick samples were obtained and a digital image analysis (DIA) of these photomicrographs was performed in order to validate and complete the MIP data. The SEM images were digitised and the Scion Image v. 4.0.2 (Scion Corporation[©], USA) software package was used to quantify changes in porosity and PSD (pores with radius larger than 0.5 μ m) following firing at different T. Three maps per brick sample with different magnification (200×, 400× and 700×) were acquired to quantify

different ranges of pore sizes. In order to perform the DIA, SEM grey-scale images were converted to binary by a thresholding process: solid parts were displayed in white and holes (i.e. pores) in black. A filter was applied performing an erosion operation, followed by dilation which smoothed objects and removed isolated pixels. Black pixels were counted and the total porosity and PSD were determined. Pore shape, spatial distribution, and connectivity were also studied using this method.

Finally, to evaluate the possible evolution of the brick porosity (e.g., development of fissures) over time once finished the firing process, which might affect the mechanical characteristics of the bricks, the ultrasound propagation velocity (V_p) was measured at pre-defined intervals and in three perpendicular directions. V_{P1} is the ultrasound propagation velocity perpendicular to the brick face, V_{P2} is the velocity perpendicular to the end and V_{P3} is perpendicular to the side. The samples used for this test were $10 \times 7 \times 3.5$ cm. The measurements (15 in each direction) were performed with a Steinkamp BP-5 ultrasound generator with 100 kHz transducers.

3. Results and discussion

3.1. Mineralogy

Table 1 displays the concentrations of the mineral phases in the raw materials and bricks determined by XRD (error of $\pm 5\%$). The concentration of non-crystalline phase (*f*) has been calculated considering the quartz contents as constant.⁴¹

Table 1

XRD semiquantitative analysis (wt.%) of non-calcareous (G) and calcareous (V) raw material and bricks fired between 700 and 1100 $^\circ C$

Sample	Qtz	Phy	Hem	Mul	Fs	Cal	Dol	Wo + Di	Gh	f
G	50	40	_	_	10	_	_	_	_	_
G7	50	40	5	_	5	_	_	_	_	_
G8	50	30	5	_	5	_	_	_	_	10
G9	50	30	5	tr	< 5	_	_	-	_	10
G10	50	_	< 10	tr	5 ^a	_	_	-	_	35
G11	50	-	10	tr	tr ^a	-	-	_	-	<40
v	40	30	_	_	5	15	< 10	_	_	_
V7	40	30	-	_	10	15	< 5	-	_	_
V8	40	25	tr	_	10	_	_	-	<10	15
V9	40	20	5	_	5	_	_	-	10	20
V10	40	_	5	_	10 ^b	_	_	< 5	10	< 30
V11	40	-	5	tr	15 ^b	-	-	< 10	5	25

Symbols after Kretz:⁷⁰ Qtz=quartz; Phy=phyllosilicates; Hem=hematite; Mul=mullite; Fs=feldspar; Cal=calcite; Dol=dolomite; Wo+Di=wollastonite+diopside; Gh=gehlenite; f=non crystalline phases. G/V: green raw material; G7/V7: fired at 700 °C; G8/V8: fired at 800 °C; G9/V9: fired at 900 °C; G10/V10: fired at 1000 °C; G11/V11: fired at 1100 °C; tr=traces; -= not present.

^a Sanidine.

^b Anorthite.

In the G raw material, quartz is the most common mineral phase; the other components are phyllosilicates and feldspars. The $< 2 \,\mu m$ fraction includes illite, smectite and low amounts of chlorite/kaolinite and paragonite. The V raw material consists primarily of phyllosilicates and quartz, with minor amounts of calcite, dolomite and feldspar. The clay fraction consists of illite, smectite, paragonite and chlorite/kaolinite. The main differences between the two types of clays are found in the $>2 \mu m$ fraction, as V has around 20% carbonates and G is lacking in carbonates. Firing causes significant changes in the phyllosilicates. At 700 °C, only dehydroxilated illite/muscovite remains, which is structurally very similar to the hydrated phase.⁴² Its amount drops as the T increases, this phase disappearing completely at T > 900 °C. All the other reflections of the clay minerals, except chlorite, vanish between 450 and 550 °C.43 Mullite is formed at the expense of illite/muscovite⁴⁴ and is detected in both brick types at about 900 °C, increasing in concentration as the T rises. Mullite is always more abundant in the G samples. Other mineral phases also increase in concentration as the T rises, such as hematite. This only occurs in the G samples, though, as in the V samples, the iron is "trapped" in the network of the calcium silicates and aluminosilicates and, therefore, the formation of hematite is inhibited.⁴⁵ New phases appear in the V samples after firing: gehlenite (a melilite group phase) appears at 800 °C, increases in concentration at 900 $^{\circ}$ C and drops at higher T; wollastonite and diopside appear at 1000 °C and increase in concentration as the firing T rises. The non crystalline phase (f) is more abundant in carbonate rich bricks (V) fired at low temperatures. However, at $T \ge 1000$ °C the trend reverts and the non carbonate bricks (G) are the most vitrified. For more details on the evolution of the bricks mineral phases see Cultrone et al.³¹

3.2. Textural evolution

SEM revealed how the shape of the pores in the bricks as well as the brick texture undergo significant changes which depend on the firing T and raw clay composition. The samples fired at 700 and 800 °C maintain the sheetlike fabric of the phyllosilicates (Fig. 1a), although the muscovite crystals show marked exfoliation along their basal planes following the loss of K⁺ and OH⁻ groups.⁴⁴ Interconnectivity between particles is limited. In addition, the V bricks show fissuring (white arrow on right in Fig. 1b), which is entirely lacking in the G samples, evidencing the first difference in the pore structure between the two brick groups. This textural difference can be accounted for by the mineralogical composition of the two groups, specifically, the carbonates in the V clay (Table 1). When the firing T exceeds 700 °C, calcite and dolomite begin to decompose, disappearing at $T \ge 870 \ ^{\circ}C^{34}$ Calcite is transformed into

calcium oxide, which occurs as extremely porous aggregates (pores <0.5 μ m) (see left side in Fig. lb). In the presence of humidity, the CaO rapidly reacts and is transformed into portlandite. This reaction is exothermal and causes a considerable increase in volume:⁴⁶

$$\operatorname{calcite}_{\operatorname{CaCO}_{3}} \stackrel{\stackrel{\operatorname{CO}_{2}}{\to}}{\stackrel{\operatorname{lime}}{\xrightarrow{\Delta T}}} \operatorname{CaO}_{AO} + \operatorname{H}_{2}\operatorname{O} \rightarrow \operatorname{Ca(OH)}_{2}$$
(1)

The dolomite decomposes in accordance with the following equation:

$$\operatorname{CaMg(CO_3)_2}_{\Delta T} \xrightarrow{\text{lime periclase}}_{\operatorname{CaO}+\operatorname{MgO}} + 2\operatorname{CO_2}$$
(2)

The MgO, in the presence of H_2O , undergoes a slow transformation into brucite and eventually into hydromagnesite, according to the following reactions:⁴⁷

$$MgO + H_2O \rightarrow Mg(OH)_2$$
 (3)

$$5Mg(OH)_2 + 4CO_2 \rightarrow Mg_5(CO_3)_4(OH)_2 \times 4H_2O$$
 (4)

The new-formed portlandite exerts a notable crystallisation pressure in the confined spaces of the brick previously occupied by CaO, producing radial fractures around the original carbonate grains.^{48,49} This is a notorious problem in ceramics made using raw materials rich in carbonates (most acute when their grain size is >1 mm) and it is known as "lime blowing".^{50,51} Such effects are less evident in the case of MgO, which hydrates very slowly.52 At 700-800 °C there is no clear evidence under SEM of partial fusion or vitrification, only sintering due to solid state reactions among adjacent crystals is observed and results in a slight porosity reduction (see below). Nonetheless, the XRD data point to the presence of non-crystalline phases (Table 1). Since the sintering rate is proportional to the particle size,⁵³ it can be concluded that G and V bricks are expected to undergo the same level of sintering since both raw materials have similar granulometry.³¹

Vitrification can be clearly detected when the samples are fired at 900–1000 °C. At 900 °C, the pores are still irregular and angular, but the phyllosilicates deform and tend to clump (Fig. lc). This is particularly evident in non-calcareous bricks. Other authors⁵⁴ have observed the formation of fine glass filaments obstructing or filling the smaller pores in non-calcareous clays fired at the same *T*.

TEM images of muscovite crystals evidence exfoliation along the basal planes at 700–800 $^{\circ}$ C due to dehydroxilation (Fig. 2a). The development of incipient ellipsoidal gas bubbles within the phyllosilicates is also observed at 800 $^{\circ}$ C (Fig. 2b). The formation of melt



Fig. 1. SEM photomicrographs of G and V samples fired at: (a) 700, (b) 800, (c) 900, (d) 1000 and (e) 1100 °C. See text for details.

pools within mica crystals that include nanometer-sized mullite crystals is observed at 900–1000 °C (Fig. 2c). A large number of mullite crystals grow within the melt at $T \ge 1000$ °C (Fig. 2d), when partial fusion of the mineral grains is significant.

At 1000 °C the phyllosilicate surfaces become smoother and the pores become ellipsoid with smooth edges. These effects are less pronounced in the samples made of calcareous clay (V, Fig. 1d) than in the silicate-rich ones (G, Fig. 1d). In fact, calcite and dolomite act as flux at low T (see f amounts in Table 1), but they are not as effective in promoting vitrification at high T,^{55,56} favouring rather a stable structure up to 1050 °C.⁵⁴ This occurs due to the incorporation of silica and alumina in the structure of new, high-temperature phases such as gehlenite, diopside and wollastonite (see Table 1) that hamper the formation of an

aluminosilicate melt.57 The fact that vitrification is more extensive in the non-carbonate samples at higher T can also be explained if we take into account that the G clays have a higher proportion of phyllosilicates compared to the V clays (Phy in Table 1). As indicated by Brearley and Rubie,58 these phases can release notable amounts of H₂O upon dehydroxylation, thus inducing melting. This is consistent with our TEM observations revealing first melting within dehydroxilating phyllosilicates (i.e. muscovite). As T increases, particle interconnectivity causes a reduction in porosity. At 1100 °C, there is extensive vitrification in all the samples, regardless of the starting mineralogical composition; the pores coalesce and become spherical ("cellular structure",⁵⁹ Fig. 1e) due to the partial or total melting of the clay particles in the matrix and the release of gases.^{60,61}



Fig. 2. Representative bright-field TEM images of phyllosilicate (muscovite, Ms) textural and phase transformations following (non-calcareous) brick firing: (a) Ms crystal showing exfoliation along (001) basal planes following dehydroxilation at 800 °C; (b) Ms crystals with ellipsoidal "bubbles" formed along (001) basal planes (800 °C); (c) high resolution lattice fringe image of a Ms crystal (oriented with (001) perpendicular to the image plane) with melt pools developing along (001) planes. Note the oriented growth of prismatic mullite (Mul) crystals within the melt pools (brick fired at 900 °C); (d) Ms pseudomorph partially transformed in an aggregate of Mul crystals embedded in melt (1000 °C). For details on the composition and *T*-evolution of these phases see Rodriguez-Navarro et al.⁴⁴

3.3. Hydric behaviour

Table 2 presents the hydric parameters of each brick type versus the firing T. The free water absorption test (Al) evidences how the samples fired at 1100 °C absorb the least amount of water (Fig. 3a), and they do so quite slowly (i.e. having the lowest absorption coefficient, Ac). However, whereas the G bricks systematically absorb less water and at a slower rate as the firing T increases, the V bricks show the highest Al and Ac in samples fired at intermediate T (V8, V9 and V10, Fig. 3a). This appears to be due to the presence of microcracks and fissures in the latter bricks as previously indicated. To evaluate the degree of pore interconnectivity (Ax) and its modification with firing, the free water absorption (Al) was compared with the forced water absorption (Af) values using the following equation:

$$Ax = \frac{Af - Al}{Af} \times 100$$
(5)

As the interconnectivity between the pores diminishes, the difference between Af and Al increases. Therefore, Ax suggests the existence of pores of difficult access (e.g., bubbles in the cellular structure⁵⁹) that are not easily accessible under natural conditions (only under forced water absorption), which indicates, to a certain extent, the degree of melt development in the bricks, at least for those fired at high T. In fact, the highest Ax values are found in samples fired at the highest T. However, if we examine the evolution through the full range of T, it can be seen that in the V samples the lowest Ax values are found between 800 and 1000 °C. This is apparently due to the presence of fissures associated to "lime blowing".⁵¹ Conversely G samples show a continuous Ax rise with increasing T. The highest values (at 1000 and 1100 °C) are indicative of a good development of the vitreous phase, as confirmed by the melt development (f) data in Table 1. The drying test reveals that the G bricks lose water faster, at any T, compared to the respective V samples (Di, Table 2). Moreover, the water loss of G bricks is faster the higher the firing T, while in the V bricks the same only occurs with the samples fired at the lowest and highest T (V7 and V11, Fig. 3b). Of these two extremes, only V11 reaches drying index values (Di) comparable to those of G samples.

These results denote a better quality of the G bricks since, the lower the absorption coefficients (Ac) and drying index (Di), the lower the negative influence of water on the bricks. As a consequence, higher durability can be expected¹⁴ as demonstrated experimentally by our group (i.e. submitting this bricks to salt crystallisation and freeze-thaw tests).⁶² It must be remembered that the drying index is calculated as a function of the time necessary to obtain the full drying of the samples,³⁹ but it does not give the absolute rate (i.e. the slope of the drying curve) at which one sample dries with respect to another. To determine the rate at which the bricks dry it is necessary to examine the evolution of the drying curve for the samples. The curves in Fig. 3b are different. All of the G samples have straight slopes parallel to each other in the first section. This phase corresponds to the constant drying rate,⁶³ where porous structure of the brick has no significant influence on the drying. The drving evolution changes where the slope peaks (critical moisture content 63) due to the type of pores and the degree of interconnectivity, after which the slow drying (falling drying rate⁶³) of samples begins. The figure reveals that the drying process of the G bricks is dominated by the constant drying rate (the straight section of the slopes is decidedly longer than in the V samples). This circumstance seems to be due to the formation of relatively large, uniform pores, as revealed by DIA and MIP (see below). In samples V8, V9 and V10, the drying is mainly controlled by the falling drying rate period due to the presence of large and small pores connected by fissures and microcracks.⁶³ The curve of V11, however, is comparable to those of the G bricks.

This behavioural "anomaly" in samples V8, V9 and V10 is primarily due to the transformation of calcite (or dolomite) into CaO (or CaO+MgO), creating a highly porous system with very small pores⁶⁴ (see Fig. 1b). This circumstance causes greater water absorption and slower drying.⁶⁵ Samples V7 and V11 have the lowest values of free water absorption and drying index because of the lack of microcracks and/or micropores (here referred as those with radius <1 μ m). At 700 °C

Table 2	
Hydric parameters of non-calcareous (G) and calcareous (V) bricks fired a	it different 2

	G7	G8	G9	G10	G11	V7	V 8	V9	V10	V11
Al	24.29	24.84	23.15	14.94	9.85	21.35	25.58	23.69	25.39	18.72
Af	24.85	25.14	23.90	16.76	12.51	21.80	25.60	23.71	25.49	21.96
Ax	2.25	1.19	3.14	10.86	21.26	2.06	0.08	0.08	0.39	14.75
Ac	0.088	0.097	0.078	0.053	0.033	0.078	0.107	0.098	0.104	0.075
Di	0.071	0.079	0.061	0.053	0.037	0.166	0.328	0.326	0.239	0.058
$P_{\rm a}$	38.63	39.28	37.41	27.49	19.45	36.14	40.13	36.97	40.58	31.21
$\rho_{\rm a}$	1.58	1.58	1.61	1.83	1.97	1.67	1.60	1.60	1.60	1.65
С	3.30	3.19	3.05	2.50	1.84	2.96	3.20	3.09	2.92	2.66

(V7), the *T* of transformation of calcite to calcium oxide has not yet been reached. In the case of V11, the high degree of vitrification at 1100 °C (revealed by SEM, TEM and XRD) counters the expansion force exerted by the portlandite; furthermore, the calcium silicates form a reaction ring that replaces the CaO (or CaO+MgO) aggregates.³¹ As suggested by Laird and Worcerster,⁵⁰ the latter effect could account for the absence of fissures in these bricks, since lime-blowing would not occur due to the development of the "ring" of aluniinosilicate phases around the calcium oxide grains, thus preventing the access of water vapour and reducing the amount of free reactive CaO (or MgO).



Fig. 3. Free water absorption (a), drying (b) and capillarity (c) curves of the G and V bricks over time.

The differences in the hydric behaviour of G and V bricks have been further confirmed by capillarity tests. The G bricks fired at the highest T showed the lowest water contents at the end of the test (Fig. 3c), with the other samples also showing an inverse relationship between water content and firing T. In the V bricks, sample V11 absorbed the least water, followed by V7, with the remaining samples all absorbing larger amounts of water.

In the G bricks, as mentioned, the absorption and porosity (Table 2) decrease as the T increases. Continuous reduction of brick porosity upon firing at increasing temperatures is a well-known fact.¹⁰ In the V bricks, however, the porosity evolution with increasing T is far more complex. It is affected not only by the development of fissures at T between 800 and 1000 °C, but also by the different porosity system caused by the carbonate presence. In the G bricks, the open porosity (P_a) values drop by 20% between 900 and 1000 °C, indicating a significant increase in vitrification (f, Table 1) and densification (ρ_a , Table 2) of the ceramic bodies. However, in the V bricks the most significant reduction in porosity occurs between 1000 and 1100 °C.

3.4. Mercury intrusion porosimetry analysis

The different characteristics in the porosity of the G and V bricks are confirmed by MIP studies, particularly when analysing the distribution of the pore sizes. In both groups of samples the distribution of pore access radius peaks at around 1 μ m (Fig. 4), although there are appreciable differences. The MIP diagrams for the G samples show a displacement of the pore access radius towards larger sizes as the firing T increases. In fact, the larger pores continue growing, whereas the smaller ones, which are initially open, close due to the vitrification process.^{16,27} The same process takes places in the Vbricks, although only at 1100 °C; the intermediate T samples have a wider range of pore sizes and a higher percentage of small pores (down to 0.01 µm in radius). These results are consistent with SEM observations (Fig. 1b). The micropores are responsible for the slow drying of these bricks (Fig. 3b).

The differences between the pore systems of the V and G bricks are more evident if the pores are divided into two populations based on pore size, under and over 1 μ m, and their evolution is observed as a function of the firing temperature (Fig. 5). In the G bricks there is a progressive decrease in the amounts of the smaller pores and an increase in the larger pores as the *T* increases. Both in the carbonate and non-carbonate bricks, the smaller pores predominate when the firing *T* does not exceed 900 °C. However, the change towards larger pore sizes occurs at 1000 °C in the G bricks and at 1100 °C in the V bricks. At these temperatures, the larger pores comprise approximately 55% of the total in the V bricks

and 80% in the G bricks (Fig. 4), showing, in the latter case, the existence of a well-developed cellular structure due to a greater release of trapped gases (i.e. water vapour).⁵⁹

These results explain the Al, *C* and *P*_a values obtained in the hydric assays (Table 2) and are consistent with the SEM observations (Fig. 1), since the gradual reduction in absorbed water by the G samples as the *T* rises is due to a progressive closing of the smaller pores caused by the advancing vitrification of the samples and the formation of large, isolated pores. In the V bricks, similar values were obtained for absorption and porosity up to 1000 °C, with scarcely any changes in the porous system. However, at 1100 °C the free absorption (Al) and the open porosity (*P*_a) abruptly dropped due to an increase in the vitrification, while the pore size increased ($r > 1 \mu m$) in the so-called cellular structure.⁵⁹

3.5. Digital image analysis

Figs. 6 and 7 show DIA results of V and G brick samples, respectively. The pore-size range analysed was $0.5 \le r \le 15 \ \mu\text{m}$. PSD histograms of G and V bricks evidence a systematic increase in pore size as T rises. This is consistent with the previous results (i.e. MIP analysis). Nonetheless, DIA of brick samples helps to complete MIP results and to overcome some of the limitations of the latter technique.

Non-carbonate bricks fired at 700 (G7) and 800 °C (G8) have a significant amount of pores with $3-7 \mu m$ in radius. G8 also has abundant pores with 7-9 µm in radius. At 900 °C (G9), when melting begins, a significant increase in the amount of pores with $r > 7 \ \mu m$ occurs and the coalescence of the pores in specific areas is observed. At lower T pores were scattered and more evenly distributed (e.g., see binary images of G7 and G8 samples in Fig. 6), although some preferred orientation of elongated pores is detected (most probably associated to the layering of phyllosilicates). At 1000 $^{\circ}$ C (G10), pores become larger and rounder following the development of a cellular structure, those with $r > 15 \ \mu m$ increasing their abundance. The smaller pores tend to disappear, particularly those with $9-15 \mu m$ in radius. It is assumed that the larger, less angular pores developed at the expense of the smaller. At 1100 °C (G11) pores with $r > 15 \ \mu m$ are the most abundant and their connectivity is significantly reduced.

Bricks with carbonates (Fig. 7) show less drastic porosity changes upon T rise (particularly in the 700– 1000 °C interval) than bricks without carbonates. At 700 °C (V7) most common pores are those with 1–5 μ m in radius. Pores are evenly distributed in the ceramic paste and almost no pore is bigger than 11 μ m. Pores with larger radius appear at 800 °C (V8). Fig. 7 evidences this change. PSD remains almost unchanged at 900 °C (V9). Pores with lager radius appear at 1000 °C,



Fig. 4. MIP pore size distribution curves [i.e. log differential intruded volume (ml/g) vs. pore radius (μ m)] of G and V bricks fired between 700 and 1100 °C.

although no significant change in pore shape or distribution is detected. In fact, pores neither reach the size of those in sample G10 nor concentrate in specific areas. Limited coalescence of pores occurs at 1100 °C (V11), but PSD is not unimodal as in G11.

Table 3 compares porosity data obtained by means of hydric tests, MIP and DIA. Differences in porosity are quite significant in some cases. This seems to be mainly due to the limitations of each measurement technique. For example, in the case of MIP large pores connected to the exterior through small ones (i.e. "ink bottle" pores) are recorded as small pores.¹¹ This explains why the volume of pores with $r < 1 \mu m$ is systematically greater for MIP than that calculated by the difference between forced water absorption and DIA porosity results. Note also that differences between MIP results and those from the other two techniques minimise as firing T of the samples increases. This is consistent with the increase in pore size and subsequent porosity reduction experienced as T rises. On the other hand, it should be noted that the DIA of SEM photomicrographs does not provide reliable information of pores with $r < 1 \mu m$, which explains why the total porosity values calculated using this technique are systematically smaller than those determined using the other two techniques. Nonetheless, DIA porosity values of higher T bricks (i.e. when most pores have $r > 1 \mu m$ and a cellular structure has developed) match those obtained by MIP and water absorption.

3.6. Ultrasound measurements

100

80

60

40

20

0

700

Vol. of pores (%)

Ultrasound measurements at different time intervals were carried out until stable values were obtained. A longer period was required for the V samples due to variations of their physical characteristics over time. The V_{P2} and V_{P3} velocity values were always higher than V_{P1} . This circumstance is due to the orientation of

Ô

1100



800

900

T (°C)

1000

the phyllosilicates parallel to the largest face of the brick. Therefore, their location perpendicular to the direction of propagation of the ultrasound waves $V_{\rm Pl}$, produces a laminar anisotropic structure in the bricks. V_{P2} and V_{P3} , in turn, can provide variable results depending on the orientation of the clay with respect to the sides of the mould used to shape it and, therefore, of the planar minerals with respect to the transducers. The first set of measurements was performed 24 h after firing. Samples V and G show similar behaviour, although the values of V_P at 700, 800 and 900 °C are systematically higher in V (Table 4). Due to the presence of carbonates, these bricks have a lower melting T (eutectic Al₂O₃-SiO₂-CaO),⁶⁶ producing the formation of larger amounts of melt at relatively low T and of denser minerals (gehlenite) as was confirmed by XRD results (Table 1). Otherwise, the little difference in the values of open porosity (P_a) could not satisfactorily explain the afore-mentioned variation in $V_{\rm P}$. However, at higher T (>900 °C), the $V_{\rm P}$ values of the G bricks equal or exceed those of the V bricks, possibly due to the fact that calcite and dolomite limit the development of melt and the subsequent densification at high T. Therefore, fand $P_{\rm a}$ values balance out. Finally, at the highest T (1100 °C), the V_P values of G bricks are similar to or slightly higher than V again. This fact could be due to the greater amount of higher-density mineral phases in V (Wo=2.9 g/cm³ Di=3.3 g/cm³ Gh=3.03 g/cm³ and, moreover, the Qtz $\alpha = 2.53$ g/cm³), despite the open porosity being significantly higher in V than in G $(P_a = 31.21\%$ and $V_{P1} = 2596$ m/s in V11 and $P_{\rm a} = 19.45\%$ and $V_{\rm P1} = 2415$ m/s in G11).

It was also found that the anisotropy values calculated from $V_{\rm P}$ fall when the firing *T* increases, which seems logical if we assume that, at high *T*, the phyllosilicates have transformed into other mineral phases (e.g., mullite + melt as evidenced by the TEM analysis) and thus the laminar morphology is lost. Note also that angular pores, which are oriented along specific brick planes (i.e. along the phyllosilicates basal planes) as revealed by DIA analysis, become smooth shaped and spherical, thereby contributing to a more isotropic $V_{\rm P}$ behaviour.

With the passage of time, the V_P differences between the two types of samples become more marked. In the G bricks, the values are the same after a month; superposing the curves reveals only small differences accountable for by the limitations of the method itself (Fig. 8), and therefore the test was ended. In contrast, in the V bricks, V_P varies quite erratically over time. This behaviour is ascribed to the degradation of the samples caused by the development of fissures due to the transformation of calcium oxide to portlandite [Eq. (1)] and finally to calcite (cabonation) and, also, because the new mineral phase has a lower density [CaO = 3.345 g/cm³; Ca(OH)₂ = 2.23 g/cm³]. This process, furthermore, does



Fig. 6. DIA of SEM photomicrographs. The pore-size distribution histograms of non-calcareous bricks (G) fired at 700–1100 °C, as well as the corresponding DIA porosity (P_t) data and binary images (pores in black) are presented.



Fig. 7. DIA of SEM photomicrographs. The pore-size distribution histograms of calcareous bricks (V) fired at 700–1100 °C, as well as the corresponding DIA porosity (P_t) data and binary images (pores in black) are presented.

Table 3

	$P_{\rm MIP}$	P _{Hydric}	$P_{\rm DIA}$	MIP	Hydric-DIA
		nyano		i	r<1 μm
G7	35.40	38.63	13.57	86.55	64.87
G8	33.87	39.28	17.61	86.37	55.16
G9	35.46	37.41	24.84	63.85	33.60
G10	34.32	27.49	21.68	27.53	21.13
G11	25.77	19.45	20.36	21.43	4.68
V 7	34.94	36.14	17.62	96.26	51.25
V8	35.97	40.13	21.91	94.55	45.40
V9	35.82	36.97	19.94	94.59	46.06
V10	34.65	40.58	27.85	93.01	31.37
V11	24.20	31.21	27.65	44.73	11.41

Comparison of porosity P(%) values obtained by means of mercury intrusion porosimetry (MIP), hydric tests (Hydric) and digital image analysis (DIA)

The vol.% of pores with radius <1 µm was calculated from MIP results and by difference from Hydric-DIA porosity values.

not take place over a definite time interval, but varies from one sample to another (see Fig. 8). Nonetheless, the V_P does diminish over time except in the samples fired at 700 and 1100 °C. In the first case, this is because the carbonates are stable, while in the second it is due to the considerable vitrification that develops. The problem of fissuring due to "lime blowing" can be solved for instance by submerging the bricks in water. This was verified in the laboratory with the V bricks fired at 900 °C; the lime is rapidly slaked upon entering into contact with water and dissolves without producing any damage. Thus, the solubilization and leaching of calcium oxide leave large pores, improving hydric behaviour of the material.⁶⁷

4. Concluding remarks

Table 5 summarises the main mineralogical, textural, and pore-system differences between the two brick types (i.e. with and without carbonates). It was confirmed that brick porosity and its evolution with firing T is a para-

Table 4

Ultrasonic wave velocity (m s⁻¹) of non-calcareous (G) and calcareous (V) bricks samples after 24 h firing

Sample	$V_{\rm P1}$	$V_{\rm P2}$	V_{P3}
G7	1032	1201	1483
G8	1135	1292	1560
G9	1545	2037	2090
G10	1995	2448	2706
G11	2415	2919	3012
V7	1252	1562	1575
V8	1429	1880	2199
V9	1803	2101	2069
V10	1974	2220	2555
V11	2596	2953	3018

meter directly associated to the mineralogical composition of the starting material. At 700 °C no major textural or porosity differences exist between carbonate and non carbonate bricks. At $T \sim 800$ °C the amount of the non crystalline phase (f) is higher in carbonate bricks which leads to higher particle connection and $V_{\rm P}$. However, in the presence of water (including environmental humidity) calcined carbonates significantly affect the stability of the bricks due to "lime blowing". In addition to CaO hydration to form portlandite $(Ca(OH)_2)$, the latter reacts with CO₂ to form CaCO₃ resulting in further volume increase, thus producing more fracturing. Crack development is confirmed by higher pore connectivity (Ax). Thermal decomposition of carbonates also causes the development of a microporosity that affects the durability of the bricks. Winslow et al.⁵ have shown that the development of pores smaller than 1.5 µm in radius negatively affects the brick quality due to variations in the dynamics of the water circulation within the pore system and the generation of elevated crystallisation pressures associated to soluble salts or freeze-thaw cycles, since in both cases the crystallisation pressure is inversely proportional to the pore radius.68

At 900 °C, the non-crystalline phase f is more abundant in carbonate bricks, a fact consistent with the bricks higher $V_{\rm P}$ values. Non-carbonate bricks undergo a slight reduction in pore connectivity and in the volume of pores with $r < 1 \,\mu\text{m}$. This is consistent with data given in the bibliography.^{4,16} In the case of clays with around 20 wt.% carbonates (V), a similar PSD is not reached until a T of 1000 °C. At this latter T differences among carbonate and non-carbonate bricks are still evident. Non-carbonate bricks undergo a more significant vitrification ($f \approx 10\%$ at 900 °C and $\approx 35\%$ at 1000 °C), which results in reduced pore connectivity and in the development of a "cellular structure"⁵⁹ where 70% of the pores have an access radius of > 1 μ m.

At 1100 °C non-carbonate bricks experience a further reduction in pore connectivity due to enhanced vitrification. This circumstance is due to the high water content produced by the dehydroxylation of the phyllosilicates with the *T* increase, which favours melt formation. A reduction in the amount of pores with r < 1 µm is observed, which is more significant in noncarbonate bricks.⁵⁹ f in carbonate bricks fired at 1100 °C is much lower due to the formation of high-temperature Ca (and Mg) silicates which leaves little silica or alumina as a vitreous phase, since they are incorporated in the structure of gehlenite, diopside and/or wollastonite.

In conclusion, the main problem with calcareous bricks, therefore, is the presence of large amounts of



Fig. 8. Variation of ultrasound velocity vs. time (days) of G and V bricks. The diagrams show the velocity (V1, V2 or V3) in m/s versus the firing T in $^{\circ}$ C.

Table 5

Brick type	Mineral phases	Porosity	Durability
With carbonates	• Ca (Mg) silicates • limited melt (900–1000 °C)	 ↑ Micropores (<1 μm) ↑ Cracks ("lime blowing") 	 ↓ Resistance to salt weathering and freeze-thaw cycles Loss due to ↑ micropores (ΔP=2γ/r)
Without carbonates	 ↑ Mullite + melt lst melt at 900 °C Melt ↑↑ 1100 °C 	 ↑ Macropores (> 1 µm) Porosity ↓ as T ↑ ↓ Pore interconnection 	 Extensive melting=isotropic/homogeneous texture=absence of weak planes ↑↑ Durability due to limited amount of micropores

Summary of mineralogical and physical-mechanical characteristics of calcareous and non-calcareous bricks fired at different T

 $\uparrow = high/abundant; \uparrow \uparrow = very high/very abundant; \downarrow little/reduced; \Delta P = crystallisation pressure (of a salt or ice in a pore of radius r), <math>\gamma = interfacial energy.$

small pores ($<1 \mu m$) and the formation of fissures which progresses quickly over time (i.e. ultrasound test results). The fissures, which radiate out from the portlandite grains, and the $<1 \mu m$ pores, formed by the decomposition of CaCO₃ and its transformation into CaO, result in a notable increase of the water absorption values whereas the drying is slower. In contrast, the bricks made of non-calcareous clay show a clear decrease of the water absorption values and a faster drying as the firing T increases. Fissuring does not occur in the calcareous bricks fired at 700 and 1100 °C, in the first case because the carbonates do not undergo any mineralogical changes, and in the second case because of the considerable vitrification, which counters the expansive force of the portlandite, and/or because of the formation of calcium silicate and aluminosilicate rings that completely surround the CaO crystals.⁵⁰

The measurements of ultrasound propagation velocity have been valuable for detecting differences in porosity and vitrification with respect to the firing T and to evaluate the bricks anisotropy. In short, it comprises a non-destructive procedure for evaluating the bricks technical quality. In addition, it allows the bricks mechanical-elastic properties to be evaluated as a function of time.

The DIA has been demonstrated to be an efficient technique for the analysis of the porosity of brick samples, the evaluation of PSD, and the study of pore shape and spatial distribution.²⁵ This technique both completes and helps correct results from other porosimetry techniques such as MIP.

It should be noted that, taking into account all the data on the parameters and properties of these bricks, as well as the energy costs in their manufacture, the highest-quality bricks are those made from the non-calcareous clay fired at T of around 1000 °C. In contrast, raw clay with about 20% carbonates, such as the V bricks, does not produce a good quality brick until T of close to 1100 °C.

Generally speaking, the non-calcareous clay fired at $T \ge 1000$ °C have the best hydric parameters, which are used as indicators of technical quality and durability.⁶⁹

When there are high proportions of carbonates, higher T must be reached to obtain a similar quality. Clearly, the calcareous clay fired at 800–1000 °C should not be discarded a priori since, as mentioned above, the problem of fissuring can be solved by submerging the bricks in water. Moreover, the fact that such bricks have very similar porosity values over such a wide range of firing temperatures makes possible the production of bricks with similar physical–mechanical properties.

Acknowledgements

This work has been supported by grants No. DGI-MAT2000-1457 from the Spanish government, and the Junta the Andalucía Research Group NMR 0179. One of us (G.C.) also acknowledges financial support by a Postdoctoral Marie Curie fellowship. We thank the Centro de Instrumentación Cientifica of the Universidad de Granada for technical assistance during SEM and TEM analyses and K. Laurin for the translation of the manuscript.

References

- Rodriguez Navarro, C., Técnicas de análisis del sistema poroso de un material pétreo ornamental. In *Cuadernos Técnicos "Técnicas de diagnóstico aplicadas a la conservación de los materiales de construcción en los edificios históricos*. Consejeria de Cultura, Junta de Andalucia, Seville, 1996, pp. 51–65.
- Mallidi, S. R., Application of mercury intrusion porosimetry on clay bricks to assess freeze-thaw durability. A bibliography with abstracts. *Constr. Build. Mater.*, 1996, **10**(6), 461–465.
- Charola, A. E. and Lazzarini, L., Deterioration of brick masonry caused by acid rain. *Am. Chem. Soc.*, 1986, 250–258.
- Lu, G., Max Lu, G. Q. and Xiao, Z. M., Mechanical properties of porous materials. J. Porous Mater., 1999, 6, 359–368.
- Winslow, D. N., Kilgour, C. L. and Crooks, R. W., Predicting the durability of bricks. *Am. Ceram. Soc. for Testing Materials*, 1988, 527–531.
- Maage, M., Frost resistance and pore size distribution in bricks. Mater. Struc., 1984, 17, 345–350.
- 7. Winkler, E. M., Stone in Architecture: Properties, Durability. Springer Verlag, Berlin, 1994.

- Kaneuji, M., Winslow, D. N. and Dolch, W. L., The relationship between an aggregate pore size distribution and its freeze thaw durability in concrete. *Cement Concrete Res.*, 1980, **10**, 433–441.
- Robertson, W. D., Evaluation of the durability of limestone masonry in historic buildings. In *Science and Technology in the Service of Conservation*, ed. N. S. Bronimelle and G. Thomson. The International Institute for Conservation of Historic and Artistic Works, London, 1982, pp. 51–55.
- Whiteley, P., Russman, H. D. and Bishop, J. D., Porosity of building materials. A collection of published results. *J. Oil Col. Chem. Assoc.*, 1977, **60**, 142–150.
- 11. Diamond, S., Mercury porosimetly. An inappropriate method for the measurement of pore size distributions in cement-based materials. *Cement Concrete Res.*, 2000, **30**, 1517–1525.
- 12. Warren, J., *Conservation of Brick*. Butterworth Heinemann, Oxford, 1999.
- Valdeón, L., Esbert, R. M. and Grossi, C. M., Hydric properties of some Spanish building stones: a petrophysical interpretation. *Mater. Issues Art Archaeol.*, 1993, 3, 911–916.
- Esbert, R. M., Ordaz, J., Alonso, F. J., Montoto, M., Gonzalez Limón, T. and Alvarez de Buergo Ballester, M., *Manual de diagnosis* y tratamiento de materiales pétreos y cerámicos. Collegi d'Apparelladors i Arquitectes Tècnics de Barcelona, Barcelona, 1997.
- Singer, S. S. and Singer, F., *Industrial Ceramics*. Chapman and Hall, London, 1963.
- Delbrouck, O., Janssen, J., Ottenburgs, R., Van Oyen, P. and Viaene, W., Evolution of porosity in extruded stoneware as a function of firing temperature. *Appl. Clay Sci.*, 1993, 7, 187–192.
- Parras, J., Sanchez Jiménez, C., Rodas, M. and Luque, F. J., Ceramic applications of middle Ordovician shales from central Spain. *Appl. Clay Sci.*, 1996, **11**, 25–41.
- Whittemore, O. J. and Halsey, G. D., Pore structure characterization by mercury porosimetry. In *Advances in Materials Characterization*, ed. D. R. Rossington, R. A. Condrade and R. L. Snyder. Plenum Press, New York, 1983, pp. 147–157.
- Fabbri, B., Gualtieri, S. and Santoro, S., L'altenativa chamotte/ calcite nella ceramica grezza: prove tecniche. In 1^a Giornata di archeometria della ceramica: Il contributo delle analisi archeometriche allo studio delle ceramiche grezze e comuni. Il rapporto forma/funzione/impasto, ed. S. Santoro Bianchi and B. Fabbri. University Press, Bologna, 1997, pp. 183–190.
- Hall, C., Of, W. D. and Prout, W., Sorptivity-porosity relations in clay brick ceramic. *Am. Ceram. Soc. Bull.*, 1992, **71**, 1112– 1116.
- Bogahawatta, V. T. L. and Poole, A. B., Strength porosity mullite content relationships for kaolinitic clay bodies containing lime additive. *Brit. Ceram. T.*, 1991, **90**, 184–189.
- Sveda, M., New look at mathematical relationships among physical properties of brick products. *Brit. Ceram. T.*, 2000, **99**, 181–186.
- Rodriguez Navarro, C. and Sebastian, E., Técnicas de análisis del sistema poroso de materiales pétreos ornamentales: usos y limitaciones. *Ingenieria Civil*, 96, 130–142.
- Abell, A. B., Willis, K. L. and Lange, D. A., Mercury intrusion porosimetry and image analysis of cement-based materials. J. Colloid Interf. Sci., 1999, 211, 39–44.
- Cerepi, A., Humbert, L. and Burlot, R., Petrophysical properties of porous medium from petrographic image analysis data. *Colloids Surface A*, 2001, **187-188**, 233–256.
- Adriani, G. F. and Walsh, N., Physical properties and textural parameters of calcarenitic rocks: qualitative and quantitative evaluations. *Eng. Geol.*, 2002, 67, 5–15.
- Orts, M. J., Escardino, A., Amorós, J. L. and Negre, F., Microstructural changes during firing of stoneware floor tiles. *Appl. Clay Sci.*, 1993, 7, 193–205.
- 28. Orkoula, M. G. and Koutsoukos, P. G., Dissolution effects on

specific surface area, particle size, and porosity of Penthelic marble. J. Colloid Interf. Sci., 2001, 239, 483–488.

- Marras, S. I., Ihtiaris, I. A., Hatzitrifon, N. K., Sikalidis, K. and Aifantis, E. C., A preliminary study of stress-assisted penetration in ceramic bricks. *J. Eur. Ceram. Soc.*, 2000, **20**, 489–495.
- Yates, M., Martinluengo, M. A., Cornejo, J. and Gonzalez, V., The importance of the porosity of mortars, tiles and bricks in relation to their bonding strengths. *Stud. Surf. Sci. Catal.*, 1994, 87, 781–790.
- Cultrone, G., Rodriguez Navarro, C., Sebastian, E., Cazalla, O. and de la Tone, M. J., Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral.*, 2001, **13**, 621–634.
- Dondi, M., Ercolani, G., Fabbri, B. and Marsigli, M., An approach to the chemistry of pyroxenes formed during the firing of Ca-rich silicate ceramics. *Clay Minerals*, 1998, 33, 443–452.
- Riccardi, M. P., Messiga, B. and Duminuco, P., An approach to the dynamics of clay firing. *Appl. Clay Sci.*, 1999, 15, 393–409.
- Peters, T. and Iberg, R., Mineralogical changes during firing of calcium-rich brick clays. *Ceram. Bull.*, 1978, 57, 503–509.
- Culliti, B. D., *Elements of X-ray Diffraction*. Addison-Wesley, Reading, MA, 1956.
- Rodriguez Gallego, M., Martin-Pozas, J. M. and Martin Vivaldi, J. L., Análisis cuantitativo de filosilicatos de la arcilla por difracción de rayos X: Influencia de las sustituciones isomórficas y cristalinidad. *Anu. Real Soc. Esp. Fis. Qui.*, 1968, 65, 25–29.
- Berber, D. J., Thin foils of non metals made for electron microscopy by sputter etching. *I Mater. Sci.*, 1970, 5, 1–8.
- NORMAL 7/81, Assorbimento dell'acqua per immersione totale. Capacità di imbibizione. CNR-ICR, Rome, 1981.
- 39. NORMAL 29/88, Misura dell'indice di asciugamento (Drying Index). CNR-ICR, Rome, 1988.
- NORMAL 11/85, Assorbimento d'acqua per capillarità. Coefficiente di assorbimento capillare. CNR-ICR, Rome, 1985.
- Huertas, J., Huertas, F. and Linares, J., Evolución de las fases no cristalinas en cerámicas arqueológicas por DRX. *B. Soc. Esp. Mineral*, 1991, 14, 71–78.
- Grim, R. E. and Kublicki, G., X-ray study of clay mineral reactions at elevated temperature. *B. Soc. Fr. Ceram.*, 1957, 36, 21– 27.
- Evans, J. L. and White, J., Further studies of the thermal decomposition of clays. *Brit. Ceram. T.*, 1958, 57, 298.
- Rodriguez Navarro, C., Cultrone, G., Sanchez Navas, A. and Sebastian, E., TEM study of mullite growth after muscovite breakdown. *Am. Mineral.*, 2003, 88, 713–724.
- Maniatis, Y., Simopoulos, A. and Kostikas, A., Moessbauer study of the effect of calcium content in iron oxide transformations in fired clays. J. Am. Ceram. Soc., 1981, 64, 263–269.
- Boynton, R. S., Chemistry and Technology of Lime and Limestone, 2nd edn. Wiley, New York, 1980.
- Garavelli, C. L., Liviano, R., Vurro, F. and Zinco, M., Idromagnesite nei materiali di rivestimento della chiesa ipogea di S. Maria della Grazia (Laterza, Puglia). In *Superfici delle Architetture: Le Finiture*, ed. G. Biscontin and S. Volpin. Libreria Progetto, Padova, 1990, pp. 189–197.
- Cultrone, G., Sebastian Pardo, E., Cazalla Vázquez, O. and de la Torre Lopez, M. J., Physical, mineralogical and textural features of ceramic clays from Granada province (Spain). In *Proceedings* of the 2nd Mediterranean Clay Meeting, ed. C. S. F. Gomes. Associação Portuguesa de Argilas, Aveiro, Portugal, 1998, pp. 298–303.
- Sanchez Jimenez, C. and Parras Armenteros, J., Las arcillas cerámicas de Santa Cruz de Mudela (Ciudad Real): influencia de la mineralogia en las propiedades tecnológicas. *B. Soc. Esp. Mineral*, 1998, **21**, 17–28.
- Laird, R. T. and Worcerster, M., The inhibiting of lime blowing. Brit. Ceram. T., 1956, 55, 545–563.

- 51. Butterworth, B., Lime blowing: some notes on the literature. *Brit. Ceram. T.*, 1956, **55**, 532–544.
- Webb, T. L., Chemical aspects of the unsoundness and plasticity in building limes. *The South African Industrial Chemist*, 1952, 6, 290–294.
- 53. Kingery, W. D., Introduction to Ceramics. John Wiley & Sons, New York, 1960.
- 54. Tite, M. S. and Maniatis, Y., Scanning electron microscopy of fired calcareous clays. *Brit. Ceram. T.*, 1975, **74**, 19–22.
- Everhart, J. O., Use of auxiliary fluxes to improve structural clay bodies. Am. Ceram. Soc. Bull., 1957, 36, 268–271.
- Segnit, E. R. and Anderson, C. A., Scanning electron microscopy of fired illite. *Brit. Ceram. T.*, 1972, **71**, 85–88.
- Alía, J. M., Edwards, H. G. M., Garcia Navarro, F. J., Parras Armenteros, J. and Sanchez Jiménez, C. J., Application of FT-Raman spectroscopy to quality control in brick clays firing process. *Talanta*, 1999, **50**, 291–298.
- Brearley, A. J. and Rubie, D. C., Effects of H₂O on the disequilibrium breakdown of muscovite + quartz. *J. Petrol.*, 1990, 31, 925–956.
- Tite, M. S. and Maniatis, Y., Examination of ancient pottery using the scanning electron microscope. *Nature*, 1975, 257, 122– 123.
- Freestone, I. C. and Middleton, A. P., Mineralogical applications of the analytical SEM in archaeology. *Miner. Mag.*, 1987, 51, 21– 31.
- 61. Veniale, F., Modern techniques of analysis applied to ancient ceramics. In Advanced Workshop: Analytical Methodologies for

the Investigation of Damaged Stones, ed. F. Veniale and U. Zezza. Università di Pavia, Pavia, Italy, 1990, pp. 1–45.

- Elert, K., Cultrone, G., Rodriguez-Navarro, C. and Sebastian, E., Durability of bricks used in the conservation of historic buildings—influence of composition and microstructure. J. Cultural Heritage (in press).
- Othmer, K., Encyclopedia of Chemical Technology. John Wiley & Sons, New York, 1978.
- Walker, D. D., The microscope and lime. In *Proceedings of the* 4th International Conference of Cement, Microscopy, ed. W. W. Rowe. International Cement Microscopy Association, Las Vegas, NV, 1982, pp. 21–48.
- Scherer, G. W., Theory of drying. J. Am. Ceram. Soc., 1990, 73, 3–14.
- 66. Winkler, H., *Petrogenesis of Metamorphic Rocks*. Springer-Verlag, New York, 1974.
- Cerdeno del Castillo, J., Diaz Rubio, R., Obis Sanchez, J., Perez Lorenzo, A. and Velasco Vélez, J., *Manual de patologias de las piezas cerámicas para la construcción*. AITEMIN, Toledo, Spain, 2000.
- Scherer, G. W., Crystallization in pores. Cement Concrete Res., 1999, 29, 1347–1358.
- Vos, B. H., Hygric methods for the determination of the behaviour of stones. In Unesco-Rilem International Symposium "Deterioration and Protection of Stone Monuments". UNESCO-RILEM, Paris, 1978, pp. 1–19.
- Kretz, R., Symbols for rock-forming minerals. Am. Mineral., 1983, 68, 277–279.