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Fired clay masonry units production incorporating two-phase olive mill waste (*alperujo*)

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Abstract

This work deals with the use of *alperujo*, the main residue from the two-phase olive oil extraction process, as a raw material in fired clay masonry units production. Different amounts (3, 6 and 12 wt%) of clay were substituted by *alperujo*, and the properties of the resulting ceramic units were compared to those of conventional products. Results show that a number of advantages can be obtained. At 12 wt% *alperujo* addition, masonry units present lower density (1710 kg m^{-3} compared to 1850 kg m^{-3} reference value) and higher thermal insulation effectiveness (18% reduction in the bulk of fired clay thermal conductivity). With respect to mechanical properties, the fired bending strength attained of approximately 14 N mm^{-2} is sufficiently high for this type of unit. In addition, the heating value obtained from the organic content of the added *alperujo* can cause a decrease in the heating requirements in the firing process.

Keywords: A. Extrusion; C. Thermal conductivity; D. Traditional ceramics; *Alperujo*

1. Introduction

The average oil content of olive fruits is about 20% by weight. Hence 80% of the fruit produced forms an agroindustrial waste that must be adequately handled. Olive oil is nowadays produced by either a two or three-phase extraction systems. The main difference between both extraction methods lies in the use of added water. Two-phase extraction adds no water to the extraction system, so the amount of wastewater generated is dramatically reduced compared to that originated from the three-phase technology, in which 0.6–1.3 l water/kg olives are used at the centrifugation step [1]. In Spain, the first olive oil producer in the world, over 90% of olive oil industrial facilities operate under the two-phase extraction procedure. As a result, raw olives are transformed into olive oil and an agroindustrial waste stream containing all the components present in the fruits other than oil, the so-called olive pulp, two-phase olive-mill waste or *alperujo*.

Alperujo consists of a sludge containing small pieces of crushed olive stone (15%, w/w), olive pulp (20%, w/w) and water (65%, w/w) [2]. It also contains a small, variable proportion of residual olive oil, whose extraction by organic solvents is still of economic interest. At the present time, this constitutes the main disposal method for *alperujo*, which also yields a solid residue that is used as fuel. The high water content of *alperujo*, its low oil content and the need of drying makes secondary oil extraction less attractive [3]. Other possible disposal methods for *alperujo* have been proposed [4], such as direct incorporation into soil as amendment [5], or as a biocide [6], but some toxic effects in plants and soil microorganisms have limited its application. The use of *alperujo* as a raw material for bioethanol production has also been proposed [3], although it should be integrated with the production of other value-added products because of low xylan and glucan content [7]. For example, stone pieces present in *alperujo* can be used for furfural production after high temperature dilute-acid hydrolysis [2]. Hydroxytyrosol has been found to be of the main components in the phenolic fraction of steam-exploded olive stones [8], and its production from pretreated olive cake has been proposed [9]. Composting is one of the most frequently

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proposed alternatives for *alperujo* disposal [10,11]. The physical consistency of the residue, due to its high water content and low porosity, is the main concern for this application, together with the large volume of compost to be handled.

Considering that Spain produced 6.5 million tons of olive fruit in 2009 [12], it can be deduced that *alperujo* production reached approximately 5.2 million tons. These data show that alternative bulk applications for this agroindustrial residue need to be explored, due to the large amount generated every year.

In a previous study, the use of wastewater from two-phase olive oil extraction in fired clay brick production was proposed as a disposal and valorisation method [13]. As a main result, it was concluded that replacing process water with olive oil wastewater can alleviate the environmental impacts of the olive oil extraction industry and, at the same time, result in economic savings for the brick manufacturing industry. The production of a product exhibiting similar technological properties as traditionally made bricks is an application that can act as a disposal method for a great volume of olive oil wastewater.

In a similar way, the present work deals with the use of two-phase olive mill waste, or *alperujo*, for building ceramic material production. The objective of the work is to assess (1) the use of *alperujo* as raw material in fired clay formulations, (2) the physical and mechanical properties of the new materials, and (3) the possibilities of using this application as an efficient disposal method, both from environmental and economic points of view.

Table 1
Physico-chemical characterisation of the used *alperujo* and those of the dry matter and olive stone.

Alperujo	
Dry matter (%)	36
Dry olive stone content (kg/kg *alperujo*)	0.21
Dry olive stone content (kg/kg dry *alperujo*)	0.46
Dry matter	
Higher heating value (MJ/kg)	21.90[a]/20.06[b]
Proximate analysis	
Volatile matter (%)	74.2
Fixed carbon (%)	22.1
Ashes (%)	3.7
Ultimate analysis	
C (%)	49.81
H (%)	6.47
N (%)	1.00
Olive stone	
Higher heating value (MJ/kg)	–/19.58[b]
Proximate analysis	
Volatile matter (%)	78.0
Fixed carbon (%)	21.5
Ashes (%)	0.5
Ultimate analysis	
C (%)	46.07
H (%)	7.17
N (%)	0.30

[a] Measured value.
[b] Estimated value from ultimate analysis [31].

2. Materials and methods

2.1. Clay

The clay used was provided by Cerámica Malpesa, S.A. (Bailén, Spain), a local ceramic industry. The chemical composition and the mineralogical characterisation of the clay were described in previous work [13]. In summary, the clay contains 59% phyllosilicates, 30% quartz, 9% calcite and trace amounts of dolomite and feldspars. Phyllosilicates include 60% illite, 35% kaolinite and 5% pyrophyllite. Concerning the clay chemical composition, 53.3% SiO_2, 16.0% Al_2O_3, 6.4% Fe_2O_3, 7.8% (CaO + MgO) and 0.8% TiO_2 allows it to be classified as red firing clay.

2.2. Characterisation of alperujo

Alperujo was collected from a local industry operating a two-phase olive oil extraction method. The composition of the *alperujo* depends on several factors, e.g. operation conditions, olive variety, and olive maturation grade, among others [4]. Also the characterisation of *alperujo* can include different parameters, depending on the intended use (compost production, contaminant charge reduction, soil amendment or biofuel, among others). An adequate characterisation shall include at least composition, grain size distribution, and heating power. The main physico-chemical features of the *alperujo* used are presented in Table 1. In the present work, *alperujo* was used in two ways, as received from the local olive oil industry, and milled in a colloidal horizontal mill. Grain size distribution corresponding to olive stone fragments for both *alperujo* and milled *alperujo* is shown in Table 2. Stone fragments contained in both *alperujo* types differ significantly in grain size distribution. The main fractions are (2.5–4) mm, and (0.5–0.8) mm, with 34.8% and 31.3% for *alperujo* and milled *alperujo*, respectively. Furthermore, all stone fragments in *alperujo* are greater than 1 mm, whereas in the milled *alperujo*, in the equivalent fraction, the cumulative weight retained for 1 mm stone fragments, only reaches 12.1%. As the addition rate of *alperujo* increases in the clay mixture, more holes from the stone fragment burning are expected in the fired body. When these holes are visible, they have an aesthetic effect for some kind of facing brick, but in the case of thin-web masonry units (5 mm thick) they act as a source of cracks. The prevention of the above effects due to large stones fragments and the achievement of a higher strength with a finer biomass [14] are the reasons for milling *alperujo* at high addition rates.

2.3. Extrusion trials, drying and firing of bodies

The extrusion trials were performed with one of the ceramic bodies currently being used in Cerámica Malpesa, S.A. for red facing bricks (RB). The mixture of clays was taken from the milling device of the industrial plant and was passed through shaking screens provided with 1.0 mm × 1.2 mm rectangular holes. The moisture content of the milled clay was typically 6–10%.

The ceramic body for extrusion was prepared by mixing the clay mixture with *alperujo* (AL) and fresh water (FW) in a lab

Table 2
Grain size distribution of olive stone fragments of *alperujo* as collected and milled.

Size (mm)	*Alperujo*					
	Weight percent		Cumulative weight retained		Cumulative weight passed	
	As collected (%)	Milled (%)	As collected (%)	Milled (%)	As collected (%)	Milled (%)
4–6	1.4	0.0	1.4	0.0	98.6	100.0
2.5	34.8	0.0	36.2	0.0	63.8	100.0
2.0	23.7	0.0	59.9	0.0	40.1	100.0
1.5	22.0	1.7	81.9	1.7	18.1	98.3
1.2	14.5	4.2	96.4	5.9	3.6	94.1
1.0	3.6	6.2	100.0	12.1	0.0	87.9
0.8	0.0	16.5	100.0	28.6	0.0	71.4
0.5	0.0	31.3	100.0	59.9	0.0	40.1
0.4	0.0	12.1	100.0	71.9	0.0	28.1
0.3	0.0	9.1	100.0	81.0	0.0	19.0
0.2	0.0	8.1	100.0	89.2	0.0	10.8
0.125	0.0	6.4	100.0	95.6	0.0	4.4
0.100	0.0	4.4	100.0	100.0	0.0	0.0
0.063	0.0	0.0	100.0	100.0	0.0	0.0

mixer. Three ceramic bodies were prepared with 3%, 6%, and 12% *alperujo* (namely, RB97AL3, RB94AL6 and RB88AL12), and with fresh water to achieve a final consistency of 2.4 kg/cm^2 (as measured by a 6.35 mm diameter penetrometer). In the clay body RB88AL12, the *alperujo* used was previously milled in a horizontal colloidal mill. The moisture content in the bodies ranged from 21% for the 3% *alperujo* mixture to 25% in the case of the 12% *alperujo* mixture. Barium carbonate was also added to prevent scumming during the drying of tests pieces. A rate of 1% (w/w) of barium carbonate suspension with 70% solids (w/w) was used. The time elapsed from *alperujo* and water addition to the beginning of the extrusion trial was around 2 h.

The clay mixture was extruded using a lab vacuum extruder provided with manual cutter (Verdés 050-C, Barcelona, Spain). The ceramic rectangular cross-section bars were obtained under 91–92% vacuum and were approximately 130 mm $\times$ 30 mm $\times$ 18 mm. Extruded test pieces were identified and weighed for moisture determination; finally the upper face of each test piece was indented at 100 mm spacing for later drying and firing shrinkage determination.

Extruded test pieces were dried at room temperature for about 12 h and then in an increasing temperature oven up to 110 °C in 8 h before reaching a constant weight for at least 24 h. Dried bars were fired in four trials: electric furnace at 1000, 1025 and 1050 °C, and gas-fired tunnel kiln, in a 24 h firing cycle at 1020 °C, according to the industrial firing cycle. Firing in an electric furnace at 1025 °C is equivalent to tunnel kiln firing at 1020 °C, as verified by Bullers ring firing under both cycles. A sufficient amount of test pieces were extruded, dried and fired to perform every test on six or ten-test-piece samples and the mean results were reported.

2.4. Analytical and testing methods for raw materials and end products

2.4.1. Alperujo

The volatile matter of *alperujo* was determined according to the CEN/TC 15,402 standard. The ash content was measured according to the CEN/TC 15,403 standard. The fixed carbon was calculated by subtracting the volatile matter and ashes content from 100 g dry *alperujo*. The higher heating value was determined according to UNE 164001 EX. Grain size distribution of dry olive stone fragments in: (a) *alperujo* as-received and (b) *alperujo* milled in a horizontal colloidal mill, were measured in a Retsch sieve shaker for 15 min in a 2 mm amplitude discontinuous vibration mode. Thermogravimetric analysis and differential scanning calorimetry of *alperujo* was carried out by using Mettler Toledo TGA/DSC1 type instrument.

2.4.2. Unfired and fired bodies

Unfired bodies were subjected to mineralogical and chemical analyses in order to characterise their composition as described in a previous work [13]. XRD was also performed on the fired ceramic pieces to determine the high-temperature phases and SEM was also used to study the mineral phases formed and the microstructures.

2.4.3. Additional tests for technological characterisation

Several technological properties of the test pieces were determined according to established ceramic procedures as follows:

- The consistency of the bars was measured using a ST 207 pocket penetrometer.
- The moisture content was determined by drying at 110 °C until a constant weight was achieved.
- Linear drying and firing shrinkages were measured with an indent marker.
- The mass loss on firing was determined by weighing.
- Dried and fired bar strength was evaluated by a three point modulus of rupture with a universal MECMESIN 2500N Versatest machine.
- Water absorption was calculated according to Appendix C of the UNE-EN 771-1:2003 standard.
- Fired bulk density was determined following the UNE-EN 772-13:2001 standard.

- Colour determination (CIE $L^*a^*b^*$ chromatic coordinates) was performed using a Minolta CR-300 colorimeter.

3. Results and discussion

3.1. Mineralogical and textural characterisation of fired bodies

With regard to the mineralogical composition of the fired bodies (Fig. 1), XRD diagrams show the same results for RB and RB + *alperujo*. Organic matter does not react with the mineral phases of the clay body, and the reaction products of the ashes contained in *alperujo* with RB mineral phases are not different from those formed in RB and/or are not detected by XRD. The fired mineralogical assemblage consists of mullite, cristobalite (starting from 1025 °C), feldspars, and vitreous phase, with the haematite content increasing with the rise in temperature, as can be seen in Fig. 1 comparing upper and lower diagrams.

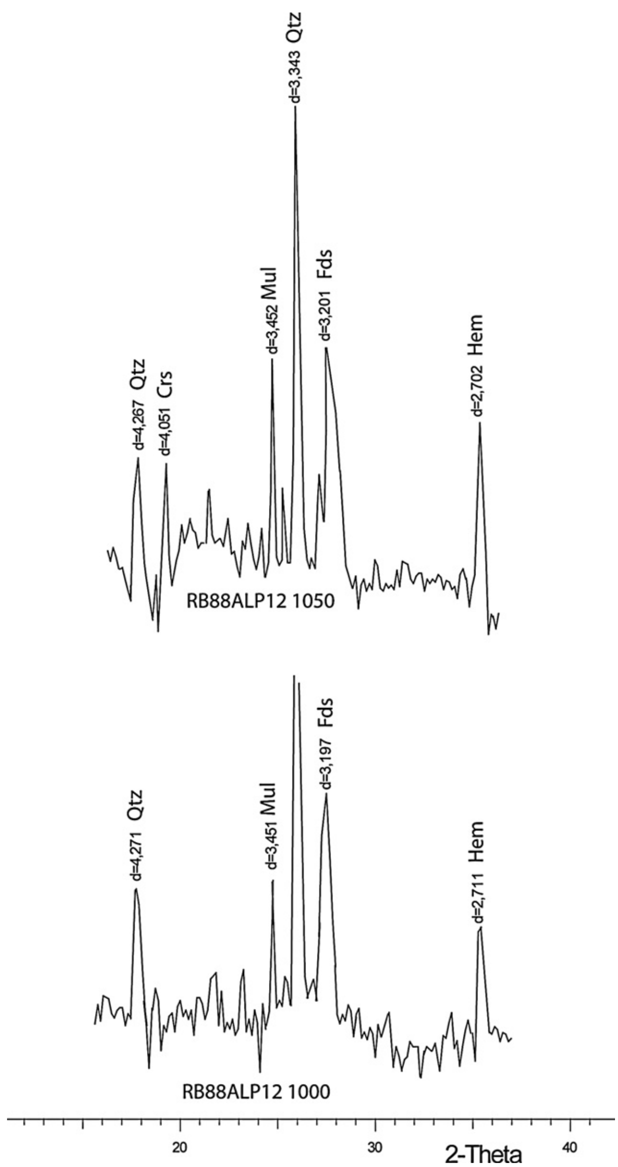

Fig. 1. X-ray diffraction patterns of RB88AL12 fired bodies at 1000 and 1050 °C. Mineral symbols, Qtz: Quartz; Crs: Cristobalite; Mul: Mullite; Fds: Feldspars; Hem: Hematite.

Alperujo behaves as an additive in the clay body, i.e. it does not change the physical-chemical properties of the pieces at a microscopic level as the substitution raw materials do. The additives only change the physical properties at a macroscopic level [15].

Regarding the SEM images, the most important feature is the higher porosity of pieces of RB + *alperujo* (Fig. 2A, B and C [RB88AL12·1050]) with pores of greater size from the combustion of organic matter compared to RB [13], where voids observed are due to the presence of carbonate clasts of the raw materials. These voids develop rims of feldspars. Around quartz clasts, feldspars are also formed from illite and calcite during firing. For firing temperatures higher than 1000 °C, a framework of vitreous filaments containing clasts of quartz and feldspars is detected (Fig. 3A and B [RB88AL12·1000]; C [RB88AL12·1025]). Also appearing frequently is the nucleus of clasts consisting of quartz with a build up of feldspars at the edge (Fig. 3D [RB88AL12·1050]).

3.2. Drying test

The test piece behaviour in drying conditions was evaluated by the Nosova index in extruded bars. The Nosova index uses the shrinkage water/porosity water ratio to determine the bodies sensitivity to drying. Nosova index values in the range of 0.5–1 indicate that the body shows little drying sensitivity; values in the range 1.0–1.5 represent average sensitivity, and a Nosova index greater than 2 is typical of very sensitive bodies which crack easily while drying [16]. The Nosova index for the RB97AL3, RB94AL6, and RB88AL12 bodies were 0.51 ± 0.06, 0.52 ± 0.02 and 0.42 ± 0.03, respectively, which allows all bodies to be classified as low sensitive bodies. This is in accordance with the fact that, as various tests show, some fibrous materials such as grasses, hemp, or paper-making sludge considerably reduce the tendency to cracking [17]. These Nosova index values are slightly lower than those obtained when using fresh water instead of *alperujo*, which averaged 0.70 ± 0.02 [13].

3.3. Thermal behaviour of alperujo

Fig. 4 shows the TG–DSC curves of *alperujo*. A total weight loss of about 98.7% was observed at 1000 °C. The first decrease in mass (1.7%) observed between 25 and 120 °C is caused by the evaporation of physical water. The second mass loss (59.3%) was observed in the 120–390 °C range which may possibly be due to the burning of volatile organic compounds (VOCs). The third and last weight loss (37.8%) observed at the upper temperature may be due to the burning of fixed carbon. In the DSC curve, there was a small endothermic reaction between 25 °C and 120 °C due to vaporisation of physical water, and two large exothermic reactions between 300 °C and 500 °C, with maxima at 340 °C and 465 °C corresponding to the burning of VOCs and fixed carbon, respectively. The exothermic reactions

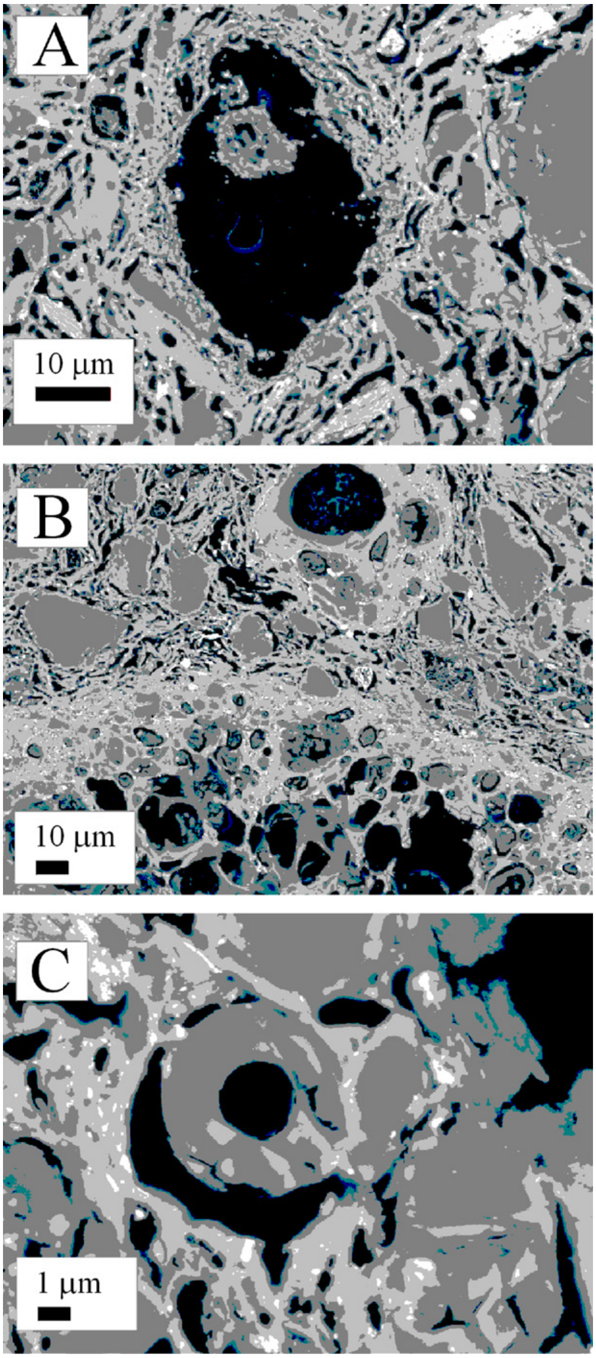

Fig. 2. Backscattered electron (BSE) images of scanning electron microscope in the atomic number contrast mode performed on polished samples from fired bodies: A, B and C [RB88AL12·1050].

usefully contribute to the thermal requirements of the kiln in the firing of masonry units that contain *alperujo*.

3.4. Dilatometric curve

The dilatometric curves for the RB, RB97AL3 and RB94AL6 bodies at 1025 °C are depicted in Fig. 5. RB88AL12 were tested in a similar way, but a black core appeared in the test probe fired in the dilatometer furnace, making the result non-representative. In general, a similar behaviour is observed for RB and RB97AL3. The RB dilatometric curve is previously analysed [13]. RB97AL3 presents as its main difference with respect to RB a slightly lower maxima expansion appearing at a lower temperature. The RB94AL6 dilatometric curve is similar to the RB and RB97AL3 until approximately 750 °C. For higher temperatures, the shrinkage associated with vitrification was stopped, and an expansion took place due to both the CO_2 release from the decomposition of the carbonate content of the bodies and the burning of the high content of organic matter. The firing cycle in the dilatometer furnace is faster than that of a tunnel kiln. As a result, the burning of the organic matter is delayed to higher temperatures in the dilatometer. At the end, the test probe RB94AL6 fired at 1025 °C in the dilatometer is approximately 0.5% higher than the test probe dry. The firing shrinkage of the clay body RB94AL6 fired in the furnace at 1025 °C is instead 0.2%. The effect of *alperujo* in firing is a reduction in shrinkage.

3.5. Technological properties of unfired bodies

The main results concerning technological properties of the unfired bodies are presented in Table 3 and are briefly discussed bellow.

3.5.1. Consistency and moisture content

The working consistency was 2.4 kg cm^{-2}; it was obtained by a moisture content of 21.3% for RB + FW body, and ranges from 21.3% to 24.9% for RB97AL3 and RB88AL12 bodies, respectively. The higher the *alperujo* content, the higher moisture content that is required to reach working consistency. Both the clay type and the pore-former agent determine the moisture content of the clay body to attain working consistency. Thus, micronized coke, paper sludge, sawdust, grass and tobacco residues are listed in order of increasing effect on the moisture content of the clay body [18,19]. While micronized coke decreases the mixing water, the other pore-former agents increase it. For addition of 12%, *alperujo* causes a medium increase in mixing water of 3.6%, lower than 4.32% dry matter added.

3.5.2. Drying linear shrinkage

Similar values were obtained for all three bodies with *alperujo* and the body without *alperujo*.

3.5.3. Dry-bending strength

The strength of RB97AL3 is similar to that of RB + FW body. However, for *alperujo* content over 3%, dry-bending strength increases with *alperujo* content and results in 34% increase for RB88AL12 compared to that for the RB + FW body. This effect is similar to that caused by some additives that enhance plasticity [20]. On the other hand, the values of dry-bending strength are high enough for the bricks to be manipulated for the usual furnace carrying systems, for which a minimum strength of 4.0 N mm^{-2} is required.

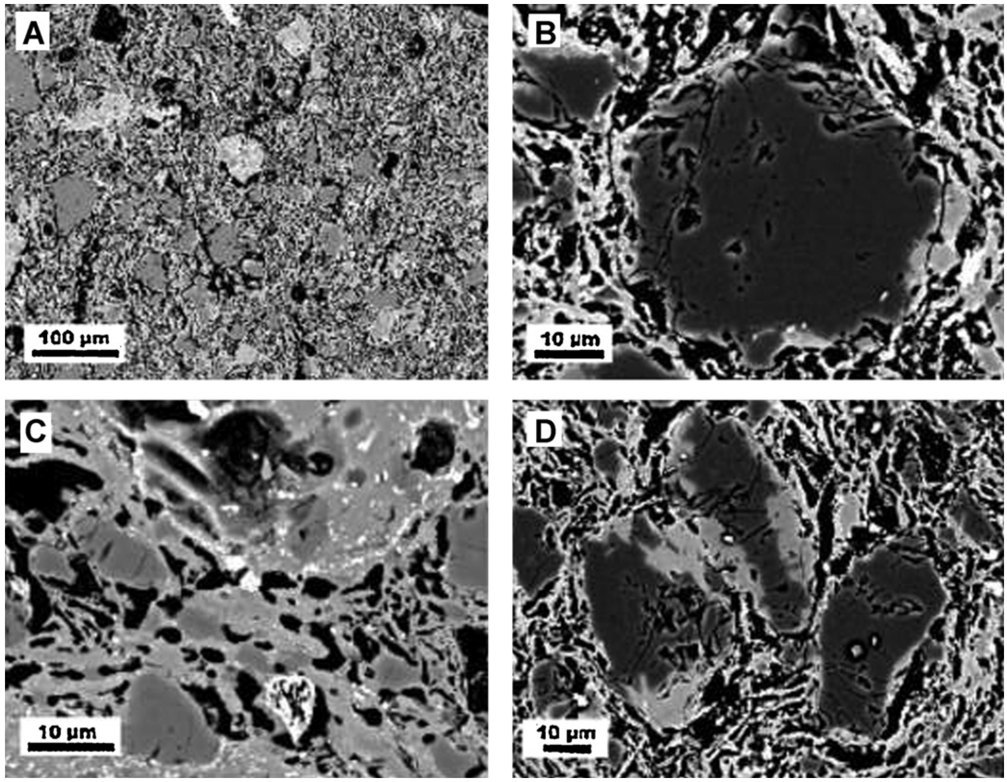

Fig. 3. Backscattered electron (BSE) images of scanning electron microscope in the atomic number contrast mode performed on polished samples from fired bodies: A and B [RB88AL12·1000], C [RB88AL12·1025], D [RB88AL12·1050].

3.6. Technological properties of fired bodies

Table 4 summarises the technological properties of RB + FW and RB + *alperujo* fired test pieces.

3.6.1. Firing linear shrinkage

Bodies formed by FW present a higher firing linear shrinkage than *alperujo* bodies at any firing temperature. This result agrees with that found in the dilatometric assays. Moreover, the linear shrinkage dependence with firing temperature is slightly higher for FW bodies.

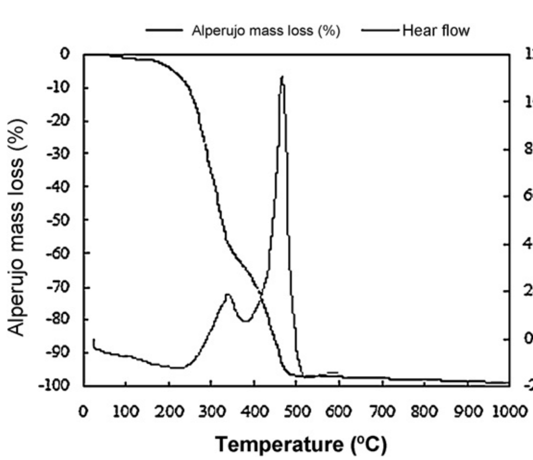

Fig. 4. Thermogravimetric analysis and differential scanning calorimetry of *alperujo*.

3.6.2. Mass loss on firing

Mass loss is due to firing reactions resulting in phyllosilicates and carbonates decomposition, organic matter combustion, and so on. The higher organic matter content of the *alperujo* bodies produces a higher mass loss at firing (52% for RB88AL12) compared to RB + FW test pieces.

3.6.3. Water absorption

The RB + *alperujo* body presents lower firing linear shrinkage and greater mass loss than the RB body; accordingly,

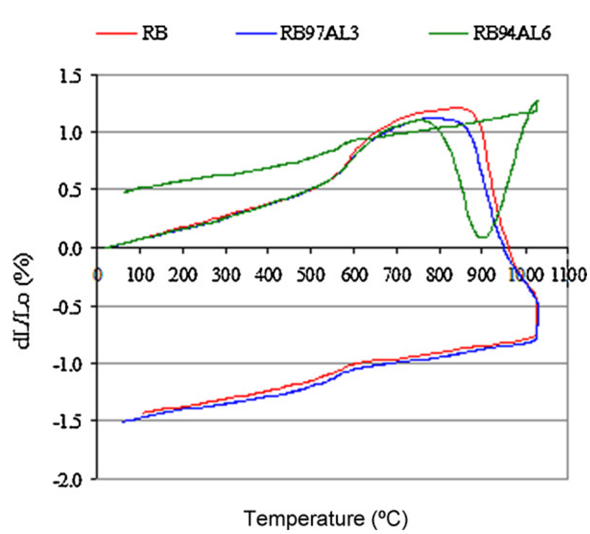

Fig. 5. Dilatometric curve for RB, RB97AL3, and RB94AL6 bodies at 1025 °C.

Table 3
Technological properties of unfired bodies.

Clay body	Firing temperature (°C)	Penetrometer consistency (kg cm^{-2})	Moisture content (%)	Drying linear shrinkage (%)	Dry-bending strength (N mm^{-2})
RB + FW (0.00% dry matter)	1000 (furnace)	2.4 ± 0.1	21.0 ± 0.2	4.6 ± 0.1	6.0 ± 0.3
	1025 (furnace)		21.0 ± 0.3	4.6 ± 0.1	
	1050 (furnace)		21.1 ± 0.2	4.6 ± 0.1	
	1020 (tunnel kiln)		21.3 ± 0.2	4.5 ± 0.2	
RB97AL3 (1.08% dry matter)	1000 (furnace)	2.4 ± 0.1	21.3 ± 0.2	4.4 ± 0.1	5.9 ± 0.8
	1025 (furnace)		21.3 ± 0.2	4.3 ± 0.1	
	1050 (furnace)		20.9 ± 0.2	4.3 ± 0.1	
	1020 (tunnel kiln)		21.1 ± 0.3	4.5 ± 0.1	
RB94AL6 (2.16% dry matter)	1000 (furnace)	2.4 ± 0.1	21.4 ± 0.1	4.1 ± 0.1	6.4 ± 0.7
	1025 (furnace)		21.4 ± 0.1	4.2 ± 0.2	
	1050 (furnace)		21.4 ± 0.3	4.2 ± 0.1	
	1020 (tunnel kiln)		21.3 ± 0.1	4.2 ± 0.1	
RB88AL12 (4.32% dry matter)	1000 (furnace)	2.4 ± 0.1	24.7 ± 0.3	4.0 ± 0.2	7.9 ± 0.4
	1025 (furnace)		24.8 ± 0.1	4.1 ± 0.2	
	1050 (furnace)		24.9 ± 0.2	4.2 ± 0.2	
	1020 (tunnel kiln)		24.8 ± 0.2	4.0 ± 0.1	

water absorption is greater in RB + *alperujo* bodies at any firing temperature. For example, for the test pieces fired in the tunnel kiln, the water absorption was 8%, 9%, 10% and 15% for RB + FW, RB97AL3, RB94AL6 and RB88AL12, respectively.

3.6.4. Fired bulk density and fired bending strength

Both of these properties decrease as the *alperujo* content in the clay body increases, as depicted in Fig. 6. In general, the fired bulk density decrease is nearly proportional to the *alperujo* content. For test pieces fired in the tunnel kiln, the higher the *alperujo* content, the higher the decrease in the fired bulk density. To allow comparisons among different pore-former agents, a new index can be introduced, i.e. the body density reducing index, BDRI (kg m^{-3}/%). This index can be defined as the ratio of the decrease in the fired bulk density to the dry matter content of the pore-former agent in the clay body. BDRI for *alperujo* in the addition range of 6–12% (2.16–4.32% dry matter) varies from 56 to 60 kg m^{-3}/% dry matter. Other pore-former agents in the range 5–7% such as sawdust, tobacco residue and grass present a higher BDRI (70, 66, and 68 kg m^{-3}/%, respectively) at 5% dry matter [18,19]. However, the mixing water for these pore-former agent added clay bodies is higher (33.0, 36.9, and 35.5%, respectively) than those of *alperujo* clay-body compositions (21.3–24.9%).

The fired bulk density decrease is nearly proportional to the *alperujo* content. Several models have been proposed to correlate the dependency of bending strength to the porosity in polycrystalline ceramic materials [21]. The porosity, the true density and the bulk density are related, so the fired bending strength can be correlated to the bulk density. Fig. 7 shows the

Table 4
Technological properties of fired test pieces.

Clay body	Firing temperature (°C)	Firing linear shrinkage (%)	Mass loss on firing (%)	Water absorption (%)	Fired bulk density (kg m^{-3})	Fired-bending strength (N mm^{-2})
RB + FW (0.00% dry matter)	1000 (furnace)	1.1 ± 0.1	7.89 ± 0.02	8	1970	16.6 ± 1.3
	1025 (furnace)	1.3 ± 0.1	7.89 ± 0.03	8	2000	19.5 ± 1.1
	1050 (furnace)	1.5 ± 0.1	7.92 ± 0.02	7	2010	19.9 ± 1.7
	1020 (tunnel kiln)	1.3 ± 0.1	7.92 ± 0.01	8	1970	18.7 ± 0.9
RB97AL3 (1.08% dry matter)	1000 (furnace)	0.4 ± 0.1	8.80 ± 0.07	10	1880	16.7 ± 2.0
	1025 (furnace)	0.5 ± 0.2	8.76 ± 0.06	9	1900	15.9 ± 1.7
	1050 (furnace)	0.7 ± 0.1	8.82 ± 0.06	8	1930	17.5 ± 2.6
	1020 (tunnel kiln)	0.9 ± 0.1	8.80 ± 0.05	9	1930	17.9 ± 1.3
RB94AL6 (2.16% dry matter)	1000 (furnace)	0.1 ± 0.1	9.74 ± 0.11	11	1820	14.2 ± 1.4
	1025 (furnace)	0.2 ± 0.1	9.74 ± 0.10	11	1840	14.1 ± 1.1
	1050 (furnace)	0.5 ± 0.1	9.73 ± 0.09	10	1870	14.3 ± 1.9
	1020 (tunnel kiln)	0.4 ± 0.1	9.78 ± 0.09	10	1850	16.2 ± 1.0
RB88AL12 (4.32% dry matter)	1000 (furnace)	0.2 ± 0.1	12.04 ± 0.02	15	1690	12.1 ± 1.9
	1025 (furnace)	0.3 ± 0.1	12.05 ± 0.02	15	1700	11.6 ± 1.4
	1050 (furnace)	0.5 ± 0.1	12.04 ± 0.0.3	14	1710	14.8 ± 1.4
	1020 (tunnel kiln)	0.6 ± 0.1	11.97 ± 0.03	15	1710	14.1 ± 1.0

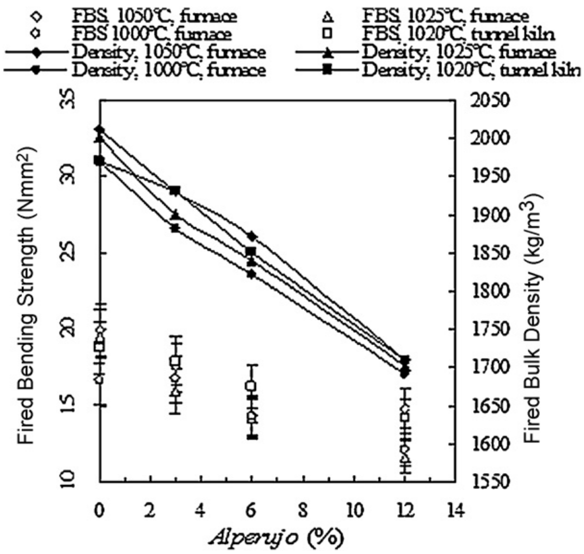

Fig. 6. Fired bending strength and fired bulk density for RB + FW and RB + *alperujo* bodies.

high dependency of fired bending strength on bulk density. The bodies fired in the tunnel kiln present a clear linear dependency of fired bending strength on bulk density.

3.6.5. Black core

Additives, such as plastic clays, are sometimes used in brick manufacturing to enhance plasticity, to increase strength or decrease cracking sensitivity. The presence of organic matter in clays can cause a firing defect known as black core should the organic carbon not be completely burnt during firing. Factors favouring black core occurrence are high organic matter content, fast firing, and the vitrification of the piece, which can hinder the combustion of the organic matter. Sometimes manganese dioxide is added to the clay body to prevent black core, but this represents an extra cost. No black core defect was detected for any RB + *alperujo* bricks, in contrast to those observed in fired clay bricks manufactured with vegetable matter (wheat seeds, soft wood, colza seeds, maize seeds, wheat straw and sunflowers seeds) [22]. In contrast to 4.32% dry matter content for RB88AL12, the higher addition rate of dry matter used by Saiah et al. [22], ranging from 5.9% to 9.1%, and an unsuitable firing cycle may be the reasons for the black core observed.

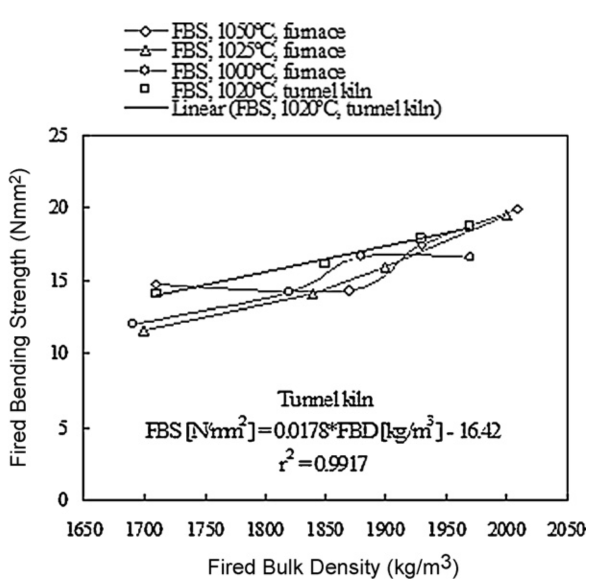

Fig. 7. Fired bending strength dependence on fired bulk density for RB + *alperujo* bodies.

3.6.6. Brick colour

Colour is an important property for masonry units used without covering like facing bricks, but is not a relevant property in units with covering such as low density clay masonry units. Table 5 shows the chromatic coordinates obtained for both body types. Values for RB + FW chromatic coordinates correspond to a deep red colour that gets darker as the firing temperature is increased; those of RB + *alperujo* correspond to orange red colour and few differences are found as a function of firing temperature, particularly for RB88AL12.

3.6.7. Thermal conductivity

Thermal conductivity is an important property of fired clay masonry units. Hence manufacturers must declare it for the products they sale on the market. Thermal conductivity of clay masonry units can be measured or estimated according to different procedures, and depends on the bulk of the fired clay conductivity, geometry and size of units. However, different ceramic bodies with the same bulk density present distinct thermal conductivities. This behaviour may be attributable to factors such as, firing temperature, mineralogical composition, the nature of the pore system, and the size and size distribution of pores [23–26].

Table 6, extracted from EN 1745:2002, illustrates the mean relationship for clay masonry units between the thermal conductivity in the dry state at a mean temperature 10 °C ($\lambda_{10, dry}$), and the bulk fired density, at percentiles $P = 50\%$, and $P = 90\%$. The decrease observed in the fired bulk density of fired bodies with the increasing addition of *alperujo* is accompanied with a decrease in the thermal conductivity. For example, in the case of bodies fired in a tunnel kiln at 1020 °C, the density of the bodies with 0%, 3%, 6% and 12% addition of *alperujo* were 1970 kg m^{-3}, 1930 kg m^{-3}, 1850 kg m^{-3} and 1710 kg m^{-3}, respectively. According to EN 1745:2002, for the above densities, the following $\lambda_{10, dry}$ thermal conductivities, 0.628, 0.612, 0.575 and 0.514 W m^{-1} K^{-1} are obtained for the bodies with 0%, 3%, 6% and 12% *alperujo* addition, respectively. To sum up, an 18% reduction in the bulk of fired clay thermal conductivity is reached when a 12% *alperujo* addition is used for a fired bulk density of 1710 kg m^{-3}, lower than that value required (1850 kg m^{-3}) for the AENOR Spanish quality mark for low density (LD) clay masonry units.

An advantage of the use of *alperujo* as a pore-former is that it is free of calcium carbonate, in contrast, for example, to other pore-formers such as paper-making sludge, so the CO_2 emissions for this additive come from the biomass. Regarding

Table 5
Colour of fired test pieces.

Clay body	Firing temperature (°C)	*L**	*a**	*b**
RB + FW	1000 (furnace)	52.5 ± 0.2	23.1 ± 0.1	25.1 ± 0.2
	1025 (furnace)	51.7 ± 0.2	22.5 ± 0.1	23.7 ± 0.2
	1050 (furnace)	50.6 ± 0.3	21.6 ± 0.5	22.3 ± 0.5
	1020 (tunnel kiln)	51.9 ± 0.2	22.1 ± 0.1	23.1 ± 0.3
RB97AL3 (1.08% dry matter)	1000 (furnace)	53.1 ± 0.2	23.3 ± 0.3	24.8 ± 0.3
	1025 (furnace)	52.4 ± 0.2	22.9 ± 0.1	24.0 ± 0.2
	1050 (furnace)	51.5 ± 0.2	21.9 ± 0.1	22.4 ± 0.1
	1020 (tunnel kiln)	52.0 ± 0.2	21.6 ± 0.5	22.4 ± 1.0
RB94AL6 (2.16% dry matter)	1000 (furnace)	53.3 ± 0.6	23.2 ± 0.3	25.2 ± 0.4
	1025 (furnace)	52.7 ± 0.3	22.5 ± 0.1	24.0 ± 0.1
	1050 (furnace)	51.7 ± 0.4	22.0 ± 0.3	23.3 ± 0.3
	1020 (tunnel kiln)	53.0 ± 0.3	22.1 ± 0.1	23.5 ± 0.3
RB88AL12 (4.32% dry matter)	1000 (furnace)	54.7 ± 0.3	22.7 ± 0.3	25.8 ± 0.5
	1025 (furnace)	54.6 ± 0.3	22.3 ± 0.3	25.1 ± 0.3
	1050 (furnace)	54.1 ± 0.2	20.8 ± 0.3	23.9 ± 0.3
	1020 (tunnel kiln)	55.8 ± 0.9	21.6 ± 0.6	24.6 ± 0.2

CO_2 emission trading, the use of biomass as a fuel is an interesting option, namely as a way to reduce the assigned quantities of CO_2, because biomass is weighted with an emission factor of 0 (t CO_2/t biomass) [27].

3.7. Higher heating value of alperujo

Clay masonry units manufacturing may sometimes include materials with variable organic matter content, like some types of clay, paper-making sludge, saw dust, polystyrene, cellulose or coke for its valuable heating value [28]. When the addition rate is sufficiently high, saw dust, paper-making sludge, cellulose, polystyrene and *alperujo* also act as pore-forming agents. Which in the case of the addition of *alperujo* results in higher heating values for bodies RB97AL3, RB94AL6, and RB88AL12 of 255, 520 and 1082 kJ/kg clay, respectively. The above heating values represent 8–25%, 17–52% and 36–108% of the heating requirements for clay masonry unit manufacturing, respectively [29]. These values are much higher than those of RB + olive oil wastewater that added 73 kJ/kg clay, equivalent to 2.4–7.3% of the heating requirement [13], depending on the building product [29]. Hence, an important proportion of thermal energy can be saved when *alperujo* is used for brick manufacturing.

Table 6
Tabulated values for the thermal conductivity in dry state at a mean temperature 10 °C ($\lambda_{10,\ dry}$) for clay masonry units.

Fired bulk density (kg m^{-3})	Clay masonry units	
	Percentile = 50%	Percentile = 90%
	$\lambda_{10,\ dry}$ (Wm^{-1} K^{-1})	
1000	0.20	0.27
1100	0.23	0.30
1200	0.26	0.33
1300	0.30	0.36
1400	0.34	0.40
1500	0.37	0.43
1600	0.41	0.47
1700	0.45	0.51
1800	0.49	0.55
1900	0.53	0.60
2000	0.58	0.64
2100	0.62	0.69
2200	0.67	0.74
2300	0.72	0.79
2400	0.77	0.84

However, the energy content of the clay body due to their biomass content must be carefully controlled. When the energy content remains below 400 kJ/kg, this energy can be completely compensated for by savings on fuel. However, when a further reduction in density, and thus in the thermal conductivity, requires high addition of biomass with an energy content higher than or equal to 1300 kJ/kg, a large deformation occurs on the firing curve [30]. As the heat is liberated at an excessive rate, local heating causes defects in the products such as cracking and spalling. If high addition of biomass is used, the oversupply of energy must be adequately managed.

Concerning the estimation of HHV of *alperujo* from ultimate analysis [31], the estimated value, 20.06 MJ/kg, is approximately 8% lower than the measured value, 21.90 MJ/kg.

3.8. Clay brick production incorporating olive mill wastewater (OMW) versus alperujo

Recently, OMW was used as a substitute for mixing water to make bricks [32]. The OMW addition was 19.5%, which represents approximately 1.1% dry matter content. Although the clay mixture, the firing temperature and some testing procedures were different than in the case of RB + *alperujo* bodies, similar trends are observed for technological properties when compared to the RB97AL3 body with 1.08% dry matter. From a technological point of view, major quality parameters affected by OMW in fired bricks were fired bulk density, fired-bending strength, water absorption and mass loss on firing. In addition, no black core was noticed using OMW.

3.9. Air pollution aspects

In the manufacturing of heavy clay products, emissions of organic substances are practically negligible even if their natural content in the clay body reaches 2%, but a problem with air pollution can arise when organic additives, both from commercial products or industrial waste, are used at additions higher than approximately 2% [33]. Thus, for example, paper-making sludge produces emissions which consist of formaldehyde, acetaldehyde, a small fraction of benzene, and an absolutely negligible fraction of polycyclic hydrocarbons. Two groups of parameters determine the organic substances emission: (1) kiln configuration (settling density, oxygen availability, firing cycle, recycling of the flue-gases within the kiln, and so on), and (2) properties of masonry units and clay body (mainly size, shape, and gas permeability of pieces and volatilization temperature of organic substances, see thermo-gravimetric analysis).

Fortunately, before resorting to flue-gas cleaning systems, optimization of the raw material composition and firing cycle is possible.

4. Conclusions

Alperujo or two-phase olive mill waste is currently the main semi-solid residue obtained in most of olive oil extraction factories which operate the so-called two-phase extraction procedure in Spain.

Experimental results show that adding *alperujo* to the clay body does not cause problems during extrusion, drying, and firing. Indeed, some technological properties like unfired bending strength are increased at high addition rates. Technological properties of units are not changed significantly when the *alperujo* addition is lower than or equal to 3%. Valorisation of *alperujo* can be achieved both in: (1) facing bricks (high density masonry units) at low addition rates as body fuel, and in (2) low density masonry units both as a body fuel and pore-former agent at an addition rate greater than 6%. A decrease in the fired bulk density from 1970 kg m^{-3} to 1710 kg m^{-3} in the clay body was attained for an *alperujo* addition rate of 12% (4.32% dry matter). Lighter units feature an estimated bulk of fired clay thermal conductivity of 0.514 Wm^{-1} K^{-1} (18% decrease), and a fired bending strength of around 14 N mm^{-2}, high enough for low density clay masonry units. In all cases, the olive oil extraction industry valorises a waste difficult to manage, while the fired clay masonry unit industry benefits from reduced heating requirements. The resulting units are equivalent to the traditional ones or exhibit lower thermal conductivity.

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