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Influence of waste addition on the porosity of clay-based ceramic membranes

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ABSTRACT

Incorporation of waste into ceramics can be an eco-friendly alternative for modification of their microstructure and related properties such as porosity, pore size and, therefore, permeability and mechanical properties. In this work, two wastes are added to a common clay mixture traditionally used for porous ceramics manufacturing: *Screen Glass*, *G*, from monitors and TV panels, and *Diatomaceous Earth*, *D*, from oil-filtering processes. Processing of the reference clay-based material (*R*) and two waste-containing formulations (10 wt.% of *Screen Glass*, *R10G*, and 10 wt.% of *Diatomaceous Earth*, *R10D*) was carried out through vacuum extrusion shaping and firing of test specimens at three maximum temperatures: 850, 950, and 1,050˚C. Final sintered specimens were characterized to determine density, bending strength, and water absorption. Microstructure was observed by SEM while pore size distribution was determined by mercury intrusion porosimetry. Permeability coefficient was calculated from these experimental parameters. Materials containing Glass waste have lower porosity and larger pore size due to partial melting of glass. As a consequence, mechanical strength of *R10G* increases around 10% due to the lower porosity while, contrary to expectations, permeability also increases due to the larger pore size. In the case of *R10D* materials, extra porosity created by oil combustion during sintering also leads to larger permeability values although a significant decrease of mechanical strength and reliability is observed.

Keywords: Ceramics; Waste valorization; Porosity; Mechanical properties; Permeability

1. Introduction

Using ceramic materials as filtering media offers a unique combination of properties such as high strength and hardness, wear and corrosion resistance, and thermal stability. In addition, control of porosity in these materials is of great interest in terms of selectivity and permeate flux for a wide range of applications [1–5]. In particular, porous clay-based ceramics, traditionally used as building materials [6,7] have lower cost and a high potential for their configuration as membranes,

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especially for fabrication of porous ceramic substrates to support intermediate and top layers [4,8–10].

Concerning ceramics processing, there is a global trend in this materials industry to consider the recycling of wastes as a new source of raw materials. In particular, clay-based ceramics can tolerate the presence of different type of waste since they are produced from natural raw materials with a very wide-ranging chemical and mineralogical composition. Thus, a wide variety of waste materials has been studied as alternative resources for their incorporation into clay ceramics [11–20].

In this context, reviews [11,12] on main experiences in waste valuation into ceramics allow identifying two groups of waste: organic ones, mainly biomass, and those with an inorganic nature. Organic waste release their calorific value during the combustion produced in the firing process for manufacturing ceramics. This combustion produces a more porous microstructure in the final ceramic products, diminishing their density [13–17].

On the other hand, inorganic wastes mostly formed by variable proportions of SiO_2–Al_2O_3–CaO, and some other minor metallic oxides, show a composition similar to that of clay raw materials. Some examples of inorganic wastes are glasses, slags, or ashes (fly or bottom) from different metallurgical industries, quarries dust, or sludge from cutting different kind of minerals like marble or granite [11,12,18–20]. These wastes can constitute the matrix of ceramic materials due to the formation of crystalline phases or to vitrification during the firing process and, thus, give rise to inertization of the waste. In this way, it is possible to get a wide range of ceramic products with very different porosities, covering from glass-ceramics to refractory ones [18–20]. Besides, valuation of these inorganic wastes allows raw materials savings and, sometimes, a lower energy consumption to obtain requested mechanical properties.

This work evaluates the addition of two kind of waste with a high SiO_2 content on the porosity and microstructure of a clay-based material with potential application as support layer in ceramic membranes. Selected waste types are *Screen Glass* from TV and monitor panels and wasted *Diatomaceous Earths* from the filtration of vegetable oils. The addition of these wastes was performed on a material containing common clays from Bailén (Southern Spain). A preliminary characterization of these ceramics comprises the determination of their main technological properties (density and mechanical strength) as well as their microstructure features and related porosity and permeability coefficients to establish their suitability for different applications.

2. Experimental

Chemical composition of selected raw materials is shown in Table 1 and has been determined by X-ray Fluorescence, Horiba XGT-5000WR for both kind of residues and Axios PW4400 in the case of the clay mixture. The *Screen Glass* waste has been encoded as *G* while the oil-impregnated *Diatomaceous Earths* residue has been called *D*. Meanwhile, the clay-based ceramic material used as a reference has been coded as *R*.

Processing of the reference ceramic material (*R*) and the two waste-containing formulations (10 wt.% of *Screen Glass*, *R10G*, and 10 wt.% of *Diatomaceous Earth*, *R10D*) was carried out through vacuum extrusion. First, all raw materials (clay and waste) were dry ground by hammer mill (sieve 3 mm). Then, the obtained power was mixed with water until achieving a consistency of 1.5 kg/cm^2 (measurement performed with a manual penetrometer, ST 207, Italy). Shaping of bars (12 cm × 2.5 cm × 1.6 cm) was carried out through vacuum extrusion (Verdés, Monobloc 050-C/OR, Spain). Sintering of these test specimens was performed in electric chamber furnace (Kittec, CBN-50, Germany) at three maximum temperatures: 850, 950, and 1,050°C, 3 h dwell.

Fired specimens were first characterized to determine bulk density and water absorption capacity according to standard test UNE-EN ISO 10545-3. A minimum of three samples were analyzed. Mechanical properties were also determined by three point bending strength tests (Hoytom, CM-C, 100 mm span) carried out using a displacement rate of 5 mm/min. A minimum of five samples were tested.

Concerning the porous microstructure, open porosity, and pore size distribution were determined by mercury intrusion porosimetry. Three specimens were analyzed. Permeability coefficient was calculated as described in [6] from laws of Darcy and Poiseuille according to the following equation:

$$K_p = \frac{r^2 \cdot \varepsilon}{8} \tag{1}$$

where K_p—coefficient of permeability (m^2); r—capillary mean radius (m); and ε—open porosity.

In addition, microstructure was observed by SEM in order to evaluate pore distribution along the specimens.

3. Results and discussion

Composition of both clay mixture and incorporated wastes is shown in Table 1. All raw materials are rich in silica and, in the case of the clays mixture is also

Table 1
Chemical composition of both types of raw materials: clay mixture and incorporated wastes

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	ZrO_2	CeO_2	Sb_2O_3	SrO	BaO	SO_3	LOI[a]
Clay mixture, *R*	56.1	13.0	5.0		2.3	7.7	0.3	3.6	0.7	0.1	0.1					0.7	10.8
Screen glass, *G*	59.0	7.1	0.6		0.2	0.2	6.8	6.5	0.5	0.1	1.6	0.2	0.3	7.9	8.5	0.1	
Diatom. earth, *D*	36.1	2.4	0.9	0.1	16.2	3.1	0.1	0.6	0.1	0.2						0.1	40.0

[a] Loss on ignition.

important to note the calcium content, associated with the presence of carbonates. As has been described elsewhere [21] for relatively similar clay and waste compositions, incorporation of these wastes is feasible for the formulation of waste-bearing porous ceramic materials. In particular, *Diatomaceous Earth*, *D*, presents a high organic fraction (loss on ignition ≈ 40 wt.%, Table 1) due to oil retention during filtering processes. Therefore, combustion of such relatively big amount of organic matter during the firing of the ceramic pieces is expected to produce more porous and lighter materials. In the case of *Screen Glass* waste, *G*, it is characterized by relatively high SrO and BaO contents, resulting in a moderate melting capacity at usual temperatures for porous ceramic production [22] and thus, only a moderate sintering promotion is expected from their incorporation into clay mixtures.

In this sense, Table 2 shows main technological properties of specimens sintered at 850, 950, and 1,050°C. First, it is noted that Glass waste incorporation causes a slight increase in density and mechanical strength of *R10G* specimens in relation to reference values of the clay mixture. For *R10D* materials, as expected, a significant density and mechanical strength decrease is observed due to the combustion of the incorporated organic matter (oily fraction). Conversely, an inverse trend is shown for the water absorption capacity of the materials (Table 2), which represents an indirect measure of their open porosity. In addition, for each composition, it should be also noted that the bulk density remains practically constant with the firing temperature and only a slight increase in density is observed for thermal treatments at 1,050°C. Similarly, the water absorption capacity undergoes very small variations (about 5%) with the firing temperature, showing a slight higher value at around 950°C.

The open porosity in the materials has been determined by intrusion porosimetry (Table 3). When the three analyzed compositions are compared, it is possible to distinguish a different behavior for each of the used residues, as expected from the technological properties analysis (Table 2). Thus, materials with *Screen Glass* waste, *R10G*, have a lower open porosity than the reference material, *R*, (Table 3) resulting in slightly higher bulk density values and lower water absorption capacity (Table 2). Meanwhile, the materials containing wasted *Diatomaceous Earth*, *R10D*, show the opposite behavior, with a higher porosity than the reference *R* material. In addition, open porosity experiences relatively low variations with firing temperature for the three studied compositions, as also described above for technology properties.

Table 2
Technological properties (density, water absorption, and bending strength) of materials sintered at different materials

Material	Firing temperature (°C)	Density (g/cm^3)	Water absorption (% H_2O)	Bending strength (MPa)
R	850	1.84 ± 0.01 (4)	15 ± 1 (4)	13 ± 1 (6)
	950	1.84 ± 0.01 (3)	17 ± 0 (3)	14 ± 1 (6)
	1,050	1.86 ± 0.02 (3)	16 ± 2 (3)	16 ± 1 (6)
R10G	850	1.90 ± 0.01 (4)	15 ± 0 (4)	14 ± 1 (6)
	950	1.90 ± 0.01 (3)	15 ± 0 (3)	17 ± 1 (6)
	1,050	1.93 ± 0.01 (3)	13 ± 0 (3)	17 ± 1 (6)
R10D	850	1.65 ± 0.02 (3)	22 ± 1 (3)	10 ± 1 (6)
	950	1.64 ± 0.03 (3)	23 ± 4 (3)	10 ± 1 (6)
	1,050	1.66 ± 0.02 (3)	22 ± 1 (3)	12 ± 1 (5)

Note: Number of tested samples is shown in brackets.

Table 3
Porosity-related properties (open porosity, mean pore radius, and permeability coefficient) of materials sintered at different materials

Material	Firing temperature (°C)	Open porosity, ε (vol. %)	Mean pore radius, r (m × 10^6)	Permeability coefficient, K_p (m^2 × 10^{14})
R	850	32 ± 1 (3)	0.4 ± 0.0 (3)	0.5 ± 0.0 (3)
	950	32 ± 1 (3)	0.4 ± 0.1 (3)	0.6 ± 0.2 (3)
	1,050	31 ± 1 (3)	0.6 ± 0.1 (3)	1.4 ± 0.3 (3)
R10G	850	30 ± 2 (3)	0.4 ± 0.0 (3)	0.5 ± 0.1 (3)
	950	31 ± 1 (3)	0.5 ± 0.0 (3)	0.9 ± 0.2 (3)
	1,050	29 ± 1 (3)	0.8 ± 0.1 (3)	2.2 ± 0.6 (3)
R10D	850	37 ± 2 (3)	0.3 ± 0.0 (3)	0.5 ± 0.1 (3)
	950	38 ± 1 (3)	0.4 ± 0.0 (3)	0.8 ± 0.1 (3)
	1,050	38 ± 1 (3)	0.6 ± 0.2 (3)	1.6 ± 1.3 (3)

Note: Number of tested samples is shown in brackets.

The above results are mainly explained taking into account the different behavior of the waste during the firing step [21]. In the case of the *Glass* waste, this material undergoes partial melting during heat treatment, resulting in a viscous phase that can fill, at least partially, smaller pores in the ceramic matrix. In the case of *Diatomaceous Earth*, the combustion of oil impregnated in this residue generates additional porosity to that present in the reference material, *R*.

The fact that material properties undergo low changes with firing temperature is typical of refractory compositions, in which increasing the sintering temperature usually results in crystallization of new phases with little formation of molten material. These new crystalline phases lead to an increase in the mechanical strength of the ceramic pieces with increasing temperatures (Table 2), whereas the low content of melting material justifies the maintenance of the total porosity and density in the material, as has been analyzed in [23,24] for common calcium containing clays. This refractory behavior usually ensures a good chemical and thermal stability for corrosive or hot effluents treatment.

A better interpretation of these results can be set from the microstructures of the materials shown in Fig. 1. Firstly, the observation of the reference material *R* treated at 1,050°C (Fig. 1(a)) shows that open porosity in this material is mainly composed of elongated pores of cylindrical type, located randomly, but uniformly distributed along grain boundaries of the different mineral phases. In addition, there is usually a large interconnection between these pores, a characteristic feature of open porosity.

In the case of materials incorporating the considered wastes, the following observations are highlighted: firstly, in the *Glass*-containing material fired at 1,050°C (*R10G*, Fig. 1(b)) appear larger pores with a more rounded shape, characteristic of a transition to

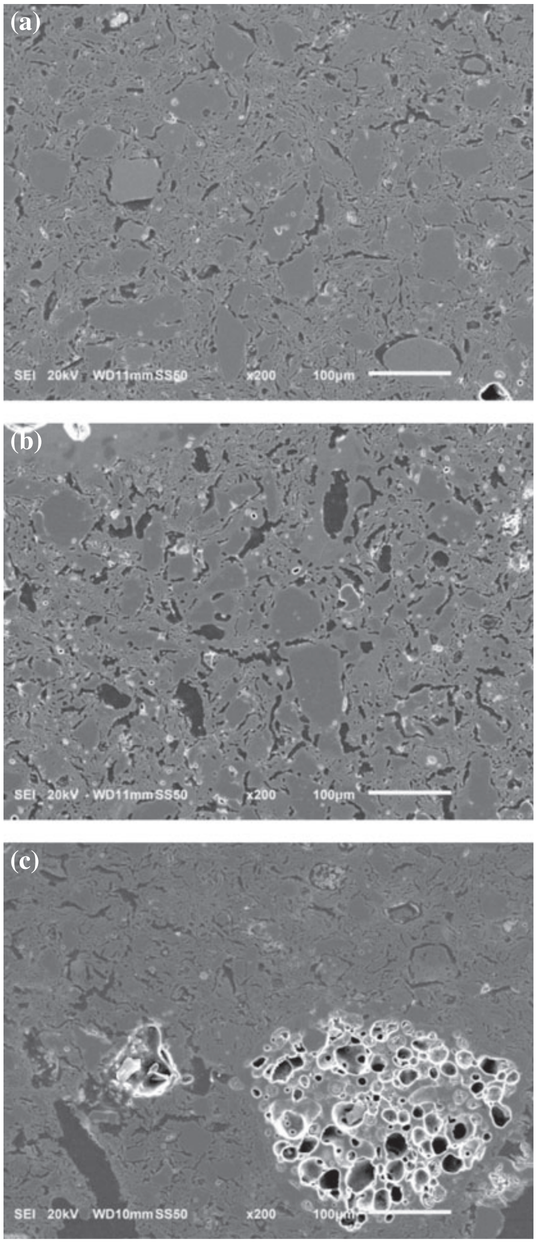

Fig. 1. SEM micrographs showing main microstructure features of specimens treated at 1,050˚C: (a) *R* material (b) *R10G* material and (c) *R10D* material.

the formation of closed porosity, and with a relatively homogeneous distribution. This microstructure is due to the closure of the smaller pores by melting glass, thanks to the contribution of melting metal oxides [18,21,22], and the own coalescence of small pores within the viscous molten phase, which leads to larger pores. This partial melting process results in the higher density and lower water absorption capacity of these materials (Table 2) but is not wide enough to modify the refractory behavior of *R10G* specimens, as has been described when analyzing the main properties evolution with firing temperature. Meanwhile, in the materials that incorporate the residue of *Diatomaceous Earth* (*R10D*, Fig. 1(c)) treated at the same temperature (1,050˚C), the first thing to note is the presence of porous substructures, with an approximate size of 100–300 μm, which are heterogeneously distributed throughout the sample. These substructures likely correspond with diatomite particles having a high pore density. These pores are predominantly rounded and due to their size and proximity have interconnection enough to be effective in increasing the water absorption capacity of these materials and decreasing their density and mechanical strength (Table 2).

Concerning pore size, Fig. 2 shows pore size distribution and Table 3 summarizes mean pore radii determined by intrusion porosimetry. For all compositions there is an evident increased pore size from 950˚C (Table 3, Fig. 2), which is in agreement with the expected trend in refractory clay materials in which new crystalline phases develop [21,23,24]. In particular, materials containing *Glass* waste have larger pore size (up to approximately 30% at 1,050˚C in relation to reference *R* clay mixture) due to partial melting of glass and the associated coalescence of small pores. In the case of *R10D* materials, no significant variations of pore size are observed, which can be attributed to the heterogeneous distribution of the additional porous substructures in this material.

As a consequence of the microstructure and properties described above, permeability coefficient (Table 3) increases in all compositions with the firing temperature due to the larger pore size, since open porosity remains almost constant. So, in the case of *R10G* samples, and contrary to expectations for a denser material, permeability coefficient significantly increases (up to 50–60% at 1,050˚C in relation to *R* clay mixtures, Table 3) due to the larger pore size, while mechanical strength increases up to 10% at 1,050˚C due to the lower porosity. In the case of *R10D* materials, even if no significant variations of pore size are observed, extra porosity created by oil combustion during sintering also leads to larger permeability values (up to 15% at 1,050˚C), although a significant decrease in mechanical strength is observed. However, any comparison of permeability values from 950˚C has to be considered only a first approximation because of the large error (Table 3) and its associated uncertainty.

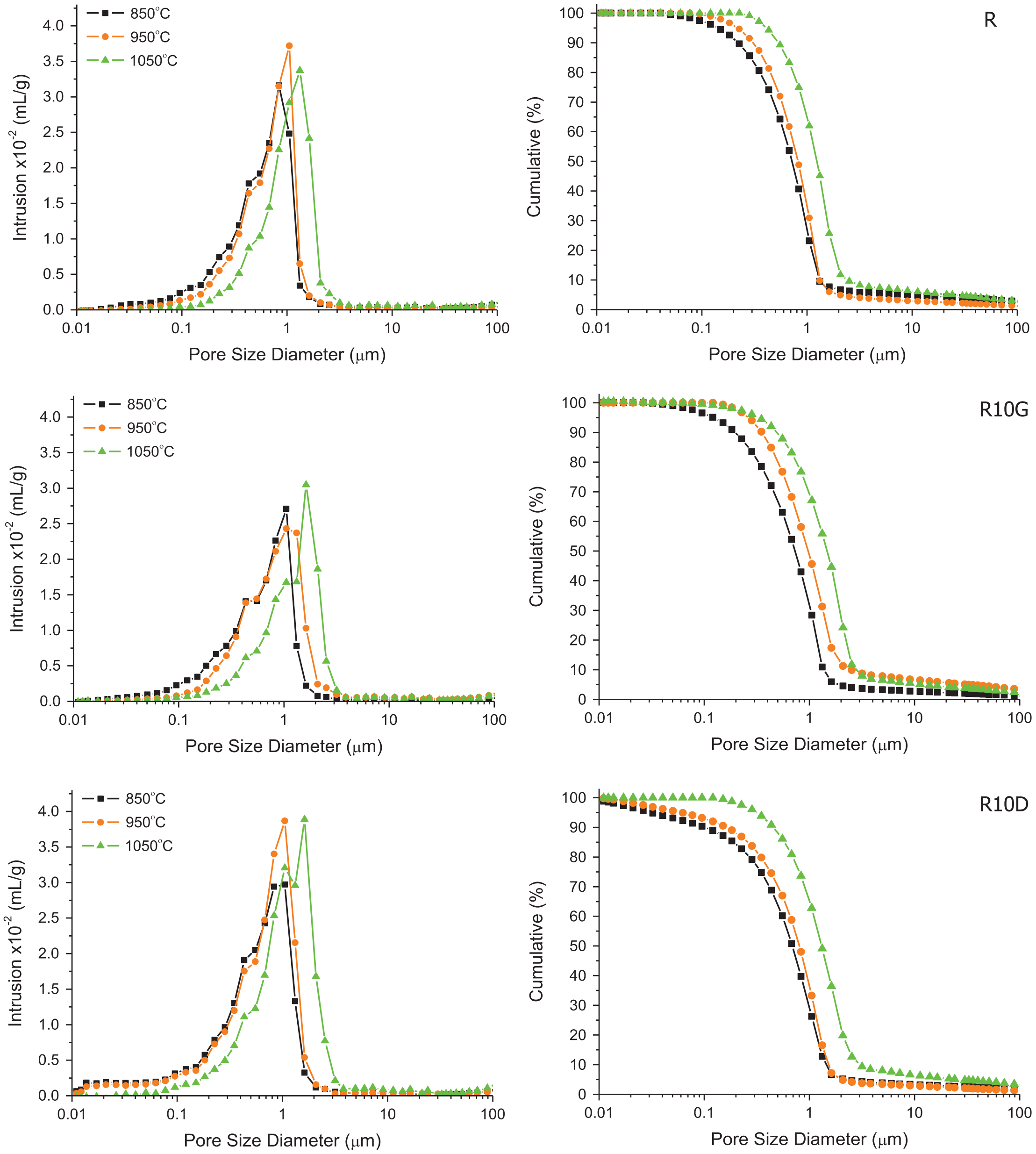

Fig. 2. Mercury intrusion porosimetry of studied materials at three firing temperatures: 850, 950, and 1,050°C.

4. Conclusions

Incorporation of waste into ceramics can be an eco-friendly alternative for modification of their porosity and related properties such as density and mechanical strength. In particular, small additions (10 wt.%) of the considered wastes: *Diatomaceous Earths* and *Screen Glass*, into clay-based materials with a refractory behavior, traditionally used by the ceramic industry, keep the small variations of their technological properties with firing temperature and, therefore, let a good control of the sintering process and final quality and stability in the ceramic pieces.

The use of *Diatomaceous Earth* causes a decrease in density and, thus, it opens the possibility of designing lighter materials. However, this residue is poorly dispersed in the ceramic matrix, which may be related to its oil fraction, being therefore necessary to optimize its processing.

The incorporation of *Screen Glass* helps materials sintering by forming additional liquid phase in a limited extension, thereby decreasing material open porosity and water absorption capacity. An increase in pore size is also observed and this causes a significant increase in the permeability coefficient. This makes the use of this residue can be of interest for the development of materials that combine larger pore sizes with adequate mechanical strength.

Furthermore, the use of waste as starting materials entails a saving of raw materials and may help to improve the life cycle of the ceramic products, thus reducing the environmental impact generated by their manufacture.

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References

[1] S. Muthukumaran, K. Baskaran, Comparison of the performance of ceramic microfiltration and ultrafiltration membranes in the reclamation and reuse of secondary wastewater, Desalin. Water Treat. 52 (2014) 670–677.

[2] Y. Lv, H. Liu, Z. Wang, S. Liu, L. Hao, Y. Sang, D. Liu, J. Wang, R.I. Boughton, Silver nanoparticle-decorated porous ceramic composite for water treatment, J. Membr. Sci. 331 (2009) 50–56.

[3] M. Sobsey, C. Stauber, L. Casanova, J. Brown, M. Elliott, Point of use household drinking water filtration: A practical, effective solution for providing sustained access to safe drinking water in the developing world, Environ. Sci. Technol. 42 (2008) 4261–4267.

[4] J.M. Benito, A. Conesa, M.A. Rodríguez, Membranas cerámicas. Tipos, métodos de obtención y caracterización (Ceramic membranes. Types, preparation methods and characterization), Bol. Soc. Esp. Ceram. Vidrio, 43 (2004) 829–842.

[5] L. Dramas, J.P. Croué, Ceramic membrane as a pretreatment for reverse osmosis: Interaction between marine organic matter and metal oxides, Desalin. Water Treat. 51 (2013) 1781–1789.

[6] M.M. Jordán Vidal, T. Sanfeliu Montolio, C. De la Fuente Cullell, Influence of temperature and composition in the mechanical resistance and porosity of ceramic pieces, Mater. Construct. 51 (2001) 5–20.

[7] M. Raimondo, M. Dondi, F. Mazzanti, P. Stefanizzi, P. Bondi, Equilibrium moisture content of clay bricks: The influence of the porous structure, Build. Environ. 42 (2007) 926–932.

[8] S. Khemakhem, R. Amara, Purification of industrial effluent by microfiltration and ultrafiltration ceramic membranes: Comparative study between commercial and elaborated Tunisian clay membranes, Desalin. Water Treat. 39 (2012) 182–189.

[9] B.K. Nandi, R. Uppaluri, M.K. Purkait, Microfiltration of stable oil-in-water emulsions using kaolin based ceramic membrane and evaluation of fouling mechanism, Desalin. Water Treat. 22 (2010) 133–145.

[10] F. Bouzerara, A. Harabi, S. Condom, Porous ceramic membranes prepared from kaolin, Desalin. Water Treat. 12 (2009) 415–419.

[11] L. Zhang, Production of bricks from waste materials—A review, Constr. Build. Mater. 47 (2013) 643–655.

[12] D. Eliche-Quesada, C. Martínez-García, M.I. Martínez-Cartas, M.T. Cotes-Palomino, L. Pérez-Villarejo, N. Cruz-Pérez, F.A. Corpas-Iglesias, The use of different forms of waste in the manufacture of ceramic bricks, Appl. Clay Sci. 52 (2011) 270–276.

[13] S.P. Raut, R.V. Ralegaonkar, S.A. Mandavgane, Development of sustainable construction material using industrial and agricultural solid waste: A review of waste-create bricks, Constr. Build. Mater. 25 (2011) 4037–4042.

[14] S. Monteiro, J. Alexandre, J. Margem, R. Sánchez, C. Vieira, Incorporation of sludge waste from water treatment plant into red ceramic, Constr. Build. Mater. 22 (2008) 1281–1287.

[15] I. Demir, Effect of organic residues addition on the technological properties of clay bricks, Waste Manage. 28 (2008) 622–627.

[16] C. Martínez, T. Cotes, F.A. Corpas, Recovering wastes from the paper industry: Development of ceramic materials, Fuel Process. Technol. 103 (2012) 117–124.

[17] J.A. De la Casa, M. Lorite, J. Jiménez, E. Castro, Valorisation of wastewater from two-phase olive oil extraction in fired clay brick production, J. Hazard. Mater. 169 (2009) 271–278.

[18] F. Andreola, L. Barbieri, A. Corradi, I. Lancellotti, CRT glass state of the art, J. Eur. Ceram. Soc. 27 (2007) 1623–1629.

[19] A. Acosta, I. Iglesias, M. Aineto, M. Romero, J. Rincón, Utilisation of IGCC slag and clay steriles in soft mud bricks (by pressing) for use in building bricks manufacturing, Waste Manage. 22 (2002) 887–891.

[20] R. Alonso-Santurde, A. Andrés, J.R. Viguri, M. Raimondo, G. Guarini, C. Zanelli, M. Dondi, Technological behaviour and recycling potential of spent foundry sands in clay bricks, J. Environ. Manage. 92 (2011) 994–1002.

[21] R.J. Galán-Arboledas, A. Merino, S. Bueno, Use of new raw materials and industrial wastes to improve the possibilities of using ceramic materials from Bailén (Jaén, southern Spain), Mater. Construct. 63 (2013) 553–568.

[22] M. Dondi, G. Guarini, M. Raimondo, C. Zanelli, Recycling PC and TV waste glass in clay bricks and roof tiles, Waste Manage. 29 (2009) 1945–1951.

[23] A. Barba, V. Beltrán, C. Feliu, J. García, F. Ginés, E. Sánchez, V. Sanz, Materias primas para la fabricación de soportes de baldosas cerámicas (Raw materials for production of ceramic tiles supports), Instituto de Tecnología Cerámica, Castellón, 2002.

[24] M.F. Serra, M.F. Acebedo, M.S. Conconi, G. Suarez, E.F. Aglietti, N.M. Rendtorff, Thermal evolution of the mechanical properties of calcareous earthenware, Ceram. Int. 40 (2014) 1709–1716.