# Evaluation of spent diatomite incorporation in clay based materials for light-weight bricks processing

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## Abstract

In this study, diatomaceous earth residues from two industrial processes, refining of vegetable oils and brewing, have been used as raw materials for brick making. The aim has been to substitute part of the clay traditionally used for the manufacturing of bricks, between 3 and 10 wt. %, with the aforementioned residues, so obtaining ceramic pieces at three firing temperatures: 850, 950 and 1050 °C. The studied properties were compared with those of conventional materials (100% clay), and the results show that these alternative raw materials can be considered technological "nutrients" whose addition improves the behavior of the materials in the drying process. The incorporation of these materials also increases the open porosity of the fired pieces and reduces the bulk density by up to 10%. The increase in porosity is greater in materials that incorporate diatoms from oil filtration, reaching the maximum value (37 vol. %). These results are confirmed from the microstructure observed by SEM. With regard to mechanical properties, increasing the content of both residues generally decreases the bending strength to values exceeding 10 MPa, thus resulting admissible for use in construction. Moreover, the energy release from the residues during the firing stage is greater than the energy demand required for drying, while the thermal conductivity values of the final materials decreases with the amount of residue, which confers thermal insulating properties to the ceramic pieces and thus can reduce the energy consumption of buildings.

**Keywords:** spent diatomite waste, clay, ceramic processing, technological properties, ceramic bricks

## 1. Introduction

Action on climate, the environment and the efficient use of raw materials and resources are important challenges that our society must face. This objective is included within the challenges of the European Union Framework Program for Research and Innovation, Horizon 2020 (ESHORIZONTE 2020) and, against this backdrop, the building sector must adapt to new materials and systems for environmentally sustainable construction. This requires research lines that reduce energy consumption as much as possible in new buildings and also seek to reduce energy consumption in buildings to be renewed (Placitelli, 2012). In fact, the energy consumption associated with construction and building materials accounts for about 40% of total energy consumed in Europe (Eco-Innovation Observatory, 2011)

Moreover, waste management, especially in the industrial and agricultural sectors, is an unresolved problem. The recycling of waste such as building materials can be an interesting solution, not only because it would reduce pollution problems, but also as an economic option in green building design. Different authors have investigated various physical, mechanical and thermal properties of bricks incorporating waste such as agricultural residues, paper, wood, plastic, ash or slag, cutting minerals powder or dry sludge from wastewater treatment plants (Barbieri et al, 2013; Bories et al, 2014. Eliche-Quesada et al, 2011; Monteiro and Vieira, 2014;

Raut et al. 2011; Zhang, 2013). Many of these works focus on the increase in porosity as a means of obtaining insulating ceramic materials.

Within the use of agricultural residues to obtain lightweight materials, Mekki et al. (2008) studied the effluents from the production of olive oil in the manufacturing of bricks, ensuring that the mechanical properties are maintained within legislative limits using percentages of up to 23 wt. % of waste. Meanwhile, Görhan et al. (2013) investigated the use of rice husk residue as a pore forming agent in final sintered materials, while more recently Aouba et al. (2016) examined the effect of the addition of organic matter from agricultural residues (olive stone flour and wheat straw residues) in improving the thermal performance of ceramic materials, maintaining the values of compressive strength. These works show that generally there is a significant positive correlation between an increase in organic matter and porosity. However, for the same percentage of incorporated waste, a different total volume of pores is created, depending on the grain size distribution. In conclusion, the pore size distribution of new materials can be controlled depending on the type and granulometry of the incorporated residue.

On the other hand, Kung et al. (2009) investigated the addition of sewage sludge from the rice industry, leading to increased porosity in the final fired clay products, and therefore to improved thermal insulation capacity, maintaining the mechanical properties within acceptable limits for the maximum percentage of residue employed (10 wt. %). Luciana et al. (2012) produced bricks from mixtures of sewage sludge from washing textiles and clay, obtaining satisfactory values for the bending strength and water absorption under Brazilian law. The results showed that this sludge can be incorporated up to a concentration of 20% by weight. Other works that include the valorization of sewage sludge are those proposed by Cusidó et al. (2011) and Qi et al. (2010).

Moreover, some mineral residues are considered suitable for making ceramics (Savoie et al., 2007; Sokolar et al., 2012; Cambronero et al., 2005) due to their low cost and their ability to cause a decrease in the temperature required for the sintering process. One of these mineral wastes is diatomaceous earth from the treatment of industrial effluents. Diatomite, diatomaceous earth or kieselgur, is a siliceous sedimentary rock composed of the fossilized skeletons of frustules of diatoms, single-celled marine algae, which accumulate by sedimentation to form large deposits. Diatomaceous earth is very light, due to its high porosity, and is chemically inert. It also has a low thermal conductivity, a high melting point, a soft abrasive capacity, a high surface area and a good absorption capacity (Arik, 2003; Khraisheh et al., 2004; Martinovic et al., 2006. Hadjar et al, 2007). All these properties mean that products with a high porous structure can be obtained, and thus 61% of the world production of diatomite is used as a filter aid, mainly in filtering sugar syrup, beer, whiskey, wine, fruit juice, water, vegetable or mineral oils and pharmaceuticals (Ediz et al., 2010). The remaining 39% is mainly applied as a filler agent in different industries, in particular paint and plastic production, but also used as an absorbent for industrial residues, bedding for pets, abrasive in polishing metal, silica additive in the manufacture of Portland cement and as raw material for the manufacture of certain thermal and acoustic insulating materials (Directorate General of Mining Development Government of Mexico, 2013; Crangle, 2014). The world's largest reserves of diatomite are in the United States (Crangle, 2014), although large deposits have also been reported in China (Lu, 1998). World production in 2013 was 2.3 Mt, with the United States of America holding 33% of total world production, followed by China with 18%, Denmark 14% and Peru 5.3%. Small amounts of diatomaceous earth are further obtained in 25 countries (Crangle, 2014).

There are different studies on the use and improvement of the physical, mechanical and thermal properties of building materials made from natural diatomaceous earth. Some authors have studied the kinetics and microstructural development of ceramics prepared with diatomite characterizing the porosity of the final product (Zhang et al., 2005). There are also studies on improving the mechanical properties of concrete made with an addition of diatomaceous earth (Ergun, 2011). Other authors have studied the improvement of mechanical and thermal properties and the chemical stability in porous ceramics prepared with the addition of natural diatoms (Martinovic et al., 2006; Al-Ghouti et al., 2007; Al-Qodaha et al., 2007; Hadjar et al., 2007; Osmanlioglu, 2007; Akhtar et al, 2009).

However, there are few investigations studying the use of spent diatoms from filtering processes. Mymrine et al. (2013) studied the use of diatomaceous earth from oil filtration and galvanic waste in the manufacture of red ceramic, obtaining products that respect the environment, with high bending strength, low levels of leaching and production costs lower than those of traditional materials. Lin and Lan (2013) investigated the retention capacity of porous ceramic adsorbents prepared with the addition of diatomaceous waste and fly ash from thermal power plants, obtaining materials with optimized adsorption and retention properties and improved thermal properties due to the porous structure formed.

Eliche-Quesada and Corpas-Iglesias (2014) studied the effects of adding spent filtration earth and spent bleaching earth from the oil refinery industry to structural ceramic materials. They proved that these residues can be used to obtain bricks with good insulating properties without losing mechanical strength and determined that the optimal percentage for both residues is 10%.

The present study shows technological, thermal and micro-structural properties of structural ceramics for construction, which in their formulation use diatoms from the refining vegetable oils and beer brewing industries as an alternative raw material to traditional clay. The research paper points specifically to the shaping of pieces by paste extrusion instead of dry pressing or with a low water content generally described in literature. Thus, the present work includes as innovation the study of the drying process of ceramic pieces, which can be crucial to the viability of brick making from the energetic and technological properties standpoint. In addition, the firing temperature range evaluated covers thermal treatments below 950 ºC (minimum operating temperature usually reported in the literature) in order to improve the energy efficiency of the proposed valorization process.

## 2. Materials and Methods

### 2.1 Materials

A clay mixture from the geographical area of Bailén (Jaén, Spain) used routinely by the ceramic industry for the production of bricks (Gallant-Arboledas et al., 2013) has been used as a reference ceramic material. Increasing quantities of weight, 3%, 7% and 10% of two types of diatomaceous earth used as filter media, one from the refining vegetable oil industry, OD, and another from the brewing industry, BD, were added to the reference clay material, R, in order to formulate the mixtures of clay and residues encodes ROD3, ROD10, D7 and RBD10.

### 2.2 Characterization Methods

### 2.2.1 Raw Materials

The chemical composition of the reference material, R, has been determined by energy dispersive XRF (PANalitical, Axios PW4400, Netherlands), with scintillation and flow detectors and Rh anode, while for the semi-quantitative determination of the mineralogical composition, X-ray diffraction equipment was used (Bruker, D8I-90, USA) with a Bragg-Brentano configuration and θ:θ geometry, a Cu anticathode and a standard scan rate of 2° 2θ/min at 30 mA and 40 kV, using the methods of disoriented powder for the total sample, and oriented aggregates for the fraction<2um.

The chemical composition of the spent diatomaceous earth, OD and BD, has been determined by wavelength dispersive X-ray fluorescence WDXRF (PANanalytical, Axios Advanced) using a Rhodium (Rh) tube with voltage 4 kW. The qualitative diffractometric analysis, XRD, of both diatoms was carried out using a Bruker D8 ADVANCE in the interval 10-80° (2θ) with a step interval of 1 second and LynxEye detector of 0.02º (2θ). The qualitative identification of the phases was made from the Powder Diffraction File references (PDF2 Release 2009).

The higher heating value (HHV) of both OD and BD was determined using an oxygen pump calorimeter (Parr, 1341 Plain) according to standard UNE 32006:1995. The lower heating value (LHV) was also obtained from this determination. A total of eight dry samples were introduced in the pump calorimeter after having been calibrated with benzoic acid.

### 2.2.2 Technological Properties

Once dry, the different R clay mixtures containing diatomaceous earth were ground in a hammer mill (Royal Triumph, H6300/1, Spain) with a 3 mm sieve then mixed with water to shape by extrusion. The amount of water added was sufficient to reach a consistency of 1.8 kg/cm$^2$, measured with a hand penetometre (Tascabili, ST 207, Italy). The different mixtures were shaped by extrusion using a lab extruder (Verdés, Monobloc 050-C/OR, Spain) reaching 90% vacuum and obtaining 120 x 28 x18 mm$^3$ test pieces and plates measuring 85 x 10 mm$^3$.

The green body characterization of the materials shaped by extrusion was carried out by determining the parameters that regulate the behavior of these materials during the drying process. For this purpose, we determined the working moisture with dry base, as well as the dry linear shrinkage by way of comparing the weight and length differences, respectively. This was done after undergoing the drying process in a forced air oven at 105±5ºC until a constant mass and length were reached. The Nosova index was also determined as this parameter shows the sensibility of a clay mixture to the dying process. The characterization of dry materials consisted of determining the parameters that condition the technical viability of these materials to be manipulated industrially in a manufacturing process. These parameters are mainly: dry bulk density determined according to the Archimedes Method and dry bending strength, determined by three point bending strength tests (Hoytom, CM-C, Spain) with a 5 kN load cell, using 100mm as the distance between the points of support and the displacement rate of 10 mm/min. A minimum of 5 test pieces were analyzed for all of these properties giving the mean values and the standard deviation as an associated error.

Dynamic sintering studies of the mixtures were carried out through a Thermal Dilatometric Analysis, using a horizontal dilatometer (Linseis, L76/1400, Germany), and Simultaneous Thermal Analysis, TGA-DSC, (Linseis, STA PT1600, Germany) up to a maximum temperature of 1050 ºC, with a heating and cooling rate of 10 ºC/min. Sintering of the shaped materials was performed in an electric laboratory furnace (Kittec CB, CBN-50, Germany) at maximum temperatures of 850ºC, 950ºC and 1050ºC for 3 hours, with a heating rate of 4ºC/min until reaching 400ºC, 2ºC/min until reaching 700ºC and 1ºC/min until reaching the maximum temperature; while the cooling process was carried out at a rate of 4ºC/min until reaching 600ºC, 2ºC/min until 400ºC and 4ºC/min until reaching ambient temperature.

Characterization of the fired materials contemplated parameters that reflect the final properties of the manufactured materials. In particular, bulk density and linear firing shrinkage were determined as per the Archimedes Method, water absorption, as per the UNE-EN ISO 10545-3 norm, while bending strength was determined in the same manner as the dry bending strength but at a displacement rate of 5 mm/min. In addition, the plates made were produced to obtain a thickness between 2-4 mm in order to establish their thermal insulation capacity, while thermal conductivity was determined using an adaptation of the hot wire method (Linseis, THB-1, Germany). A minimum of 5 test pieces were analyzed for the aforementioned properties giving the mean values and the standard deviation as an associated error.

Microstructural analysis of the fired material was carried out by combining the technique of mercury intrusion porosimetry (Micromeritics Autopore IV 9500, USA), to determine the pore size distribution in the range of 0.005 to 360 µm of equivalent diameter, with observations by scanning electron microscopy, SEM-EDX (Jeol, JSM-6010 IA, Japan) to evaluate the microstructure of the materials.

## 3. Results and Discussion

### 3.1 Characterization of Raw Materials

Tables 1 and 2 show the chemical and mineralogical composition of the mixture coded R and the diatomaceous waste from the vegetable oil refining, OD, and beer brewing, BD, industries used in this study. The chemical composition of the material coded R, traditionally used by the ceramic industry of Bailén (Jaén, Spain) is a mixture of clay with a high concentration of silicon oxide and significant amounts of aluminum oxide, iron and calcium, in addition to sodium and potassium oxide, which confer it a high melting capacity (Table 1). The high content of $SiO_2$ in the mixture corresponds to the quartz present in its mineralogical composition (Table 2), while the CaO y MgO corresponds to calcite and dolomite present in the clay. On the other hand, the predominant phyllosilicates are illite and esmectite, which confer it its fundencia capacity and the necessary plasticity to be used at an industrial level.

The diatomaceous waste from the beer brewing industry, BD, is mainly an inorganic residue (LOI < 6%, Table 1) whose chemical composition is 83.3% silicon oxide, Table 1, along with other oxides present in a minor proportion, where aluminum oxide stands out with 2.9%. From the mineralogical point of view, the amorphous phase predominates (Table 2), whilst the crystalline phases present in this waste are quartz and cristobalite, the latter in a greater proportion. Diatomaceous waste from the vegetable oil refining industry, OD, is a mixed waste, made up of an organic part, as shown in the weight loss value (40.0%) due to combustion and/or pyrolysis of the oil fraction (Table 1), and an inorganic fraction, mainly amorphous. It should also be emphasized that the organic matter content of each type of waste is consistent with their corresponding application. Hence, diatomaceous earth used for filtering vegetable oil eliminates solids in suspension and colloids that introduce turbidity in the system (Mymrine et al., 2013), while in the specific case of the beer brewing industry, diatomaceous filters are used to obtain a specific rate of clarification and delay the natural turbidity process (Canales, 2005).

To supplement the study of these types of waste, the heating power was also established through its impregnated organic load. The HHV of filtration earth from oil and beer is 2,810 and 789 Kcal/Kg, respectively. As for the LHV, the values are 2,564 and 743 Kcal/Kg. These values are in line with the organic matter content or loss on ignition shown in the chemical analysis in Table 1, much higher in the oil treatment waste.

## 3.2 Drying characterization

Table 3 shows the characterization results for the materials during the drying stage prior to the firing process. The data shows that in all the compositions, with the exception of mixture ROD7, there is an increase in the working moisture percentage needed for the shaping by extrusion; this is more evident in the materials that incorporate beer residue. However, in spite of needing more water for the shaping process, all the mixtures made with residues show lower values of dry linear shrinkage (Table 3), especially for the materials that incorporate diatomaceous earth from oil refining, OD. This is due to the fact that materials that incorporate residues in their formulation are more porous (less dense) making it easier for water to exit from the inner part of the piece when a greater capillary porosity network is formed and the tension the material undergoes during the drying process is reduced. The materials that contain OD need a smaller percentage of working moisture, compared to the materials that contain BD, and this also contributes to their reduced dry linear shrinkage.

This reduction of the dry linear shrinkage is reflected in the Nosova Index, Table 3, whose value is reduced when the waste content is increased. This indicates that the mixture of clay and residues is less susceptible to suffer pathologies associated to the drying process. Therefore, adding these residues to the reference mixture improves its behaviour during the drying process. Hence, Nosova Index values between 0.5 and 1 are a characteristic of clay materials that have a medium sensitivity to drying; while values <0.5 are characteristic to clay and/or mixtures with high porosity when dry, which dry quickly and without difficulties. [Avgustinik, 1983].

From an energy consumption standpoint, it has to be stressed that the high level of humidity needed during the shaping by extrusion process requires a considerable amount of energy to dry the pieces before firing. Considering an enthalpy of water vaporization of 540 $Kcal/Kg_{H2O}$, Table 3 shows the vaporization energy required to dry the reference materials and the different mixtures with diatomaceous residues. It is clear that the higher level of humidity in shaping the mixtures results in a greater demand of energy for drying, up to 19% higher for material R7BD. Nevertheless, this increase in energy consumption during the drying process can be balanced out when the drying and firing processes are considered globally, because, as has been previously described, during the firing stage, calorific power is released from the organic fraction of the residues. Hence, for example, for each Kg of R7BD mixture, an additional 20 kcal are needed as energy for drying; however, during the firing process, 55 kcal can be gained, taking into account the HHV of the BD residue and its incorporation to the mixture of 7% in weight.

On the other hand, when the materials that contain the OD residue are compared to the material coded R, it can be observed that there is an increase of the dry bending strength (Table 3). This is because the organic matter present in the residue (in this case oil) acts as a binder, so increasing cohesion between the particles in the mixture (Monteiro and Vieira, 2005). Alternatively, mixtures that incorporate BD undergo a decrease in the bending strength value with respect to the material coded R because this residue acts as a degreasing agent as it contains less organic matter and a greater amount of quartz and cristobalite in its composition, which reduces the cohesion of particles in the mixture. Dry bending strength values between 3.0 and 7.0 MPa are considered optimal values for clay materials intended for manufacturing ceramic products for construction. Therefore, the mixtures formulated with diatomaceous residues in this paper are deemed suitable to be manufactured at an industrial level.

### 3.3 Thermal Analysis

Figure 1 shows the main transformations experienced by the material coded R and the mixtures incorporating 10 wt. % of diatomaceous waste, R10OD and R10BD, when they undergo a thermal treatment of up to 1050ºC. Based on the evolution of the thermal dilatometric curves, Figure 1a), the thermogravimetric curves (TG Figure 1b) and the differential scanning calorimetry curves (DSC, Figure 1c), the behaviour of materials when exposed to temperature is analyzed as follows:

Between the ambient temperature and 500ºC, the thermal dilatometric curves of the materials being studied exhibit a continuous expansion, with the exception of mixture R10OD, which shows an expansion fluctuation between 200ºC and 400ºC, which is connected to the exothermic peak shown in the DSC curve (Figure 1c), due to the oxidation and/or pyrolysis of the organic matter present in the diatomaceous waste from oil, OD, whose maximum value is at 355ºC. There is a 2.8% mass weight loss associated to this exothermic peak, Figure 1b). The organic matter, present in lesser amounts in mixtures coded R and R10BD, also experiences oxidation, as is shown in the exothermic peaks of the DSC curves of both materials at 450ºC, Figure 1c), even though they do not reach the combustion intensity of the organic fraction present in the OD residue, which has a greater calorific power, as has been described previously. It should also be pointed out that the greater weight loss of sample R10BD below 200ºC can be due to a deficient drying of said sample before the analysis.

Starting at 500ºC, mixtures experience an expansion increase until approximately 600ºC, as is shown in the thermal dilatometric curves, Figure 1a), mainly due to the allotropic transformation of α quartz into β quartz shown in the DSC curve, Figure 1c), as a small endothermic peak at 573ºC. In addition, between 500 ºC and 700 ºC there is also a loss of mass, as shown in thermogravimetric curves (Figure 1b), related to the dehydroxilation of the clay mineral present in the material coded R and that is characteristic of illite (Sánchez Muñoz and Carda Castelló, 2003) which is the predominant phyllosilicates in said clay base (Table 2).

In temperatures above 600ºC, expansion gradually loses intensity until it reaches 750ºC, 720ºC and 775ºC for materials coded R, R100D and R10BD respectively, which is the moment when these materials experience their maximum expansion. This maximum expansion is inferior in the material coded ROD10, because a more porous microstructure is inevitably formed in this material after the combustion of its organic matter. Maximum expansion values between 0.85% and 1.15% are considered normal in clay and clay mixtures customarily used for clay brick manufacturing for construction (Bueno and Alvarez de Diego, 2008). Likewise, there is an endothermic reaction typical of the breakdown of the carbonates present in the mixtures in the form of calcite, Table 2, as shown in the DSC curves, Figure 1c), of the materials being studied and that have a mass loss of 4.3% for the mixtures coded R and R10OD, and 3.2% for the mixture that adds 10% of beer diatomite. The smaller loss weight of mixture R10BD when compared to mixture R is attributed to the lack of carbonates in the form of calcite from BD residue, Table 2.

An abrupt contraction of all the materials starts as of 830ºC until they reach 950ºC for the mixtures coded R and R10BD; whereas for the mixture coded R10OD it starts as of 764ºC until it reaches 900ºC. Mixture R10OD reaches the sintering temperature sooner than mixtures R and R10BD because of the greater content of alkaline-earth compounds such as MgO and CaO (Table 1), which are present in this mixture and act as melting agents in addition to producing a greater contraction. On the other hand, adding BD does not modify considerably the behavior of the reference mixture because it includes significant percentages of quartz and cristobalite (Table 2), which are inert minerals in the range of temperatures being studied (Barba et al, 2002). Contraction values inferior to 2% are typical of clay formulations used to manufacture porous ceramic materials for construction such as bricks (Bueno and Alvarez de Diego, 2008).

When the contraction process finishes, a new expansion appears in the three materials, as is shown in the dilatometric curves (Figure 1a), and the exothermic reactions of the DSC curves (detail in Figure 1c). This expansion process is more significant in mixture R10OD, followed by material coded R and the mixture that adds 10% of BD. The greater expansion in mixture R10OD is due to its greater content of MgO and CaO oxides (Table 1) which, when they react to $SiO_2$ and $Al_2O_3$ from decomposition of the phyllosilicates structure, form new crystalline phases, which cause a volumetric expansion in the samples (Barba et al., 2002; Serra et al., 2014).

Based on the data obtained from the thermal analyses and having corroborated that, from a thermal point of view, the different mixtures incorporating diatomaceous wastes are suitable for manufacturing ceramic bricks, the temperatures selected for the firing process of the materials are as follows: 850ºC, because at this temperature the contraction or sintering process has already begun and it is a typical working temperature in the brick making industry [Bueno and Álvarez de Diego, 2008]; 950ºC, because at this temperature expansion reactions are produced due to the formation of new crystalline phases; and, 1050ºC, because this is the temperature at which the neo-formed crystalline phases have fully expanded and start to melt, according to the contraction shown in the thermo dilatometric curve at 1050ºC in materials containing a residue, Figure 1a).

## 3.4 Microstructure

Figure 2 shows the microstructures of the material coded R and of the mixtures that contain 10% of the residues proposed, at the sintering temperatures selected. In the two materials containing residue, namely R10OD and R10BD, a matrix with an elongated porosity is observed, similar to that of material R, that develops when increasing the sintering temperature. This elongated porosity is typical of ceramic materials whose predominant phyllosilicate is illite (García Ten et al., 2010). The evolution of porosity caused by the sintering temperature is not only seen in the volume but also in the pore size of the reference material and the materials made with 10% of diatomaceous waste at the three sintering temperatures. As observed in said figure, when the sintering temperature increases, the pore size also increases. This can be due to the formation of calcium crystalline phases (Serra et al., 2014) and the disappearance of pores with sizes inferior to 0.2 µm, which is due to the formation of the vitreous phase that gradually seals small pores, as can be seen in the contractions shown in the thermo dilatometric curves of Figure 1a) at 1050ºC. This join action causes an increase of pore volume, mainly between 850ºC and 950ºC, as well as an increase of pore size, mainly between the temperatures of 950ºC and 1050ºC. This is especially evident in the material that contains diatomaceous waste from oil filtration, OD, which has higher calcite content (Table 2).

As well as the porosity referred to above, an additional porosity originates in material R10BD at 850 ºC – 950 ºC around the grains embedded in the ceramic matrix, caused by the appearance of fissures at the grain's edge around quartz and cristobalite, Q in EDX analysis in Figure 2, provided by the diatomaceous waste of the beer brewing industry, BD, Table 2, as shown by the microstructures of Figures 2d) and e). These fissures and grain edges become smaller as the temperature is increased because the liquid phase formed during sintering gradually seals them.

Alternatively, white structures abundant in silicate, aluminium and magnesium appear in material R10OD, F2 in Figures 2g), h) and i), which have a great amount of small circular pores and whose origin is the diatomaceous waste from oil filtration, OD, that has a significant content of Mg, Table 1. The size of those circular pores increases considerably when we increase the sintering temperature from 950ºC, Figure 2h), to 1050ºC, Figure 2i). This increase in pore size is not fully reflected in the porosimetry of Figure 3, mainly due to the heterogeneity in the distribution of these structures [Galán-Arboledas et al., 2015].

Apart from the porosity, fissures and edges of the grain in material R10BD and the white structures of material R10OD, the microstructures show the crystalline phases developed during sintering. In the three materials sintered at 950ºC, the EDX analyses show the appearance of hollow structures circled by white areas, F1 in Figures 2b), e) and h). These structures result from the breakdown of carbonates present in the mixtures (Table 2), which results in $CO_2$ being released, so creating the hollow space, and CaO, which disseminates towards the matrix and reacts with the aluminum and silicon oxides originated from the breakdown of the phyllosilicates to form silicates and calcium aluminates. This reaction, in which crystalline calcium phases are form, is shown in the thermal dilatometric curve as a volumetric expansion starting at 900ºC, Figure 1a).

### 3.5 Technological Properties

Figure 4 shows sintering diagrams of the reference material and of the mixtures formulated by adding the residues selected. In material R in particular, relatively refractory behaviour can be observed at the maximum firing temperature. In general, this behaviour displays not very relevant modifications of the main technological properties, even though it is possible to establish the following evolution of the properties. When the treatment temperature is increased from 850 to 950ºC, the density (1.84 g/ $cm^3$) and linear shrinkage (0.1 %) of the pieces remains constant; however, it is possible to observe small increases in the open porosity (from 28 to 30 vol. %) and the bending strength (13.4 and 13.7 MPa at 850 and 950 ºC, respectively). This evolution is mainly due to the formation of calcium crystalline phases, as shown in the exothermic peaks of DSC curves, Figure 1c), around 920 ºC, and the EDX spectra of Figure 2; such phases provoke a porosity increase in the materials, as shown in the porosimetry in Figure 3 at 950 ºC. Meanwhile, an additional increase of the firing temperature to 1050 ºC results in a more significant increase of the density and the firing linear shrinkage (until 1.86 $g/cm^3$ and 0.7 %, respectively). As a consequence of this densification, there is an increase of the mechanical strength (16.3 MPa), which is not apparent in the open porosity values (29 vol. %). Therefore, this behavior reflects the beginning of the vitrification or sintering process with a liquid phase that originates the densification of the pieces, but that is accompanied by an increase in the pore size (Figures 2 and 3), which allows the open porosity of the pieces to be practically stable.

Adding the proposed diatomaceous waste to the material coded R modifies its technological behavior with the firing temperature as follows: on the one hand, the mixtures that contain earth from vegetable oil filtration (series of materials coded OD) undergo a significant decrease in the density of the ceramic pieces (until a minimum value of 1.64 g/cm$^3$ for material R10OD sintered at 950 ºC). This lesser density comes from the fact that the OD residue is already porous and contains organic matter (LOI, Table 1) which, when eliminated during the sintering process, produces greater porosity in the materials that contain it in all concentrations and at all work temperatures, and can be as low as 37 vol.% in material R10OD treated at 950ºC. Also, attention should be drawn to the fact that adding this residue in low concentrations (3, 7 wt.%) produces an evolution of the properties at a temperature slightly different to that of material R; therefore, a constant increase of the open porosity of these materials is observed when the sintering temperature of said materials is increased to 1050ºC. This progressive increase occurs because in this material the fusion or vitrification process does not compensate the development of the porosity associated to the formation of crystalline phases when the temperature is increased. Its linear shrinkage value therefore decreases to negative values (until -0.4% in material R7OD at 1050 ºC); therefore, this reflects a volumetric expansion of the material, while significant increases of bending strength are not perceived. This occurs mainly because alkaline earth elements are incorporated (especially Mg) when this residue is added. On the contrary, adding 10% of this residue results in materials with lesser density and greater porosity but whose evolution has a temperature closer to that of material coded R, with a more evident densification or vitrification at 1050 ºC. This can be due to deficiently mixing this composition on account of its greater content of impregnated oil and, as it has been shown in Figure 2i), this produces a very heterogeneous microstructure with a deficient distribution of the porous diatomaceous structures.

As for the series of materials that incorporate beer brewing residue BD, the evolution of their technological properties at the sample temperature shows that, as with the oil residue, a reduction of the apparent density is observed for these mixtures when compared to the mixture coded R, until a minimum value of 1.67 g/cm$^3$ in material R7BD treated at 950 ºC. En general, there is a greater decrease in the samples that incorporate OD rather than BD because this latter residue contains less organic material (LOI, Table 1). When said organic matter is eliminated during the sintering process, it generates a smaller degree of open porosity in the materials containing it, reaching a value of 35 vol. % in material R7BD treated at 950 ºC. As for the evolution of technological properties at the treatment temperature, it can be observed that in spite of the greater porosity and therefore greater density of the pieces, the tendency of materials with a low content of residue (3,7 wt.%) is practically paralleled to that of material coded R; therefore keeping its relatively refractory character. However, material R10BD starts to show a greater tendency to vitrification that was also observed incipiently in the thermal dilatometric curves (Fig. 1a) at 1050 ºC, which produces a slight and continuous increase of the density, as well as, a constant decrease of open porosity with the firing temperature. This tendency is confirmed with the evolution of the linear shrinkage that reaches values of up to 1% in the material treated at 1050 ºC.

The values of the determined technological properties show, in general, the viability of obtaining ceramic pieces with the selected formulations and firing temperatures. In this way, the range of typical values for common ceramic bricks reaches 2% for linear shrinkage, open porosity ranges from 28 to 44 vol. %, while the bending strength is 6 to 17 MPa, although it is more common to find values between 10 and 15 MPa (Bueno and Álvarez de Diego, 2008; Fabbri an Dondi, 1995a; Fabbri and Dondi 1995b). Therefore, it can be stated that only material R10OD at low firing temperatures (850 – 950 ºC) displays a mechanical strength that is more deficient due to its high open porosity and to a bad dispersion of the oil residue.

## 3.6 Thermal Conductivity

Figure 5 shows the values for thermal conductivity of the material coded R and the materials that incorporate different quantities of diatomaceous waste at the three sintering temperatures being studied. Figure 5a) shows the conductivity changes based on the amount of residues added whereas Figure 5b) shows said evolution based on the firing treatment temperature. In general, Figures 5a) and 5b) both show that the thermal conductivity of the material coded R (0.68 – 0.70 W/mK) undergoes few changes with temperature, similar to what has already been described for the technological properties and in all the cases superior to the conductivity value of materials containing residues. This greater thermal conductivity of the material coded R is clearly related to the fact that it is the less porous material, as shown by its open porosity values (Figure 4).

Observing the behaviour of the materials that incorporate the diatomaceous waste being analyzed allows us to see that the materials that incorporate earth from oil refining, series FOD, display lower thermal conductivity, obtaining intermediate values between these values and those of material reference R for materials that incorporate residues from beer brewing, RBD, in line with the porosity values described in the previous section. Furthermore, it should be pointed out that materials RBD have a greater content of quartz (Table 2), which increases conductivity (García Ten et al., 2010).

When the amount of residue increases from 3% to 10% (Figure 5a), thermal conductivity for the mixtures is modified following two different tendencies based on the residue being added, regardless of the firing temperature used. When residue from the oil refining industry, RDO, is added, thermal conductivity is maintained or decreases when the amount of residue increases. On the other hand, if residue from the beer brewing industry, BD, is used, adding up to 7 wt.% causes a slight decrease of the thermal conductivity, whereas, if 10 wt.% of residue is added, said thermal conductivity slight increases again.

These tendencies are congruent with the evolution of the technological properties shown in the previous section. Hence, in the series of materials coded RBD, one can observe the maximum porosity for the R7BD composition (Figure 4) and, therefore, these materials display the least thermal conductivity (Figure 5a), especially when treated at 950 ºC (0.58 W/mK). In contrast, the slight conductivity increase in material R10BD when compared to that with 7 wt.% is in line with the greater capacity to vitrify observed in this material in the sintering diagrams (Figure 4). On the other hand, the decreasing evolution of the conductivity with residue OD is related to the refractory behavior and the constant increase of open porosity of the materials with a residue weight of 3 and 7 %. However, lesser conductivity of material R10OD (up to 0.45 W/mK in the material treated at 1050 ºC) does not reflect the greater vitrification capacity of this material according to the technological properties observed in Figure 4 and in the dilatometric curve of Figure 1a. This fact can be associated to the heterogeneity in the distribution of porous structures (Figure 2i), which has been mentioned before and, above all, the increase in porous size in the materials with 10 wt.% of OD residue at 1050 ºC, as it is shown in the microstructures, Figure 2 and the porosimetry, Figure 3 for the material R10OD. This occurs because when the porous size increases, continuity of the solid phase is difficult, as is the conduction of heat through the material, which is the main heat transmission mechanism, together with convection and radiation, that has a smaller influence [Mesa Rueda, ???].

When the sintering temperature is increased from 850 ºC to 950 ºC, the thermal conductivity of the materials that contain diatomaceous waste decreases (Figure 5b). Materials R3BD and R7BD exhibit the greatest decrease in thermal conductivity because they experience the greatest increase in porosity (Figure 4). When the sintering temperature reaches 1050 ºC, materials that contain OD residue undergo a decrease of their thermal conductivity value, with material R10OD showing the greatest decrease in its conductivity value. Meanwhile, materials that contain BD residue undergo an increase in their thermal conductivity value when compared to the data measured at 950ºC. As has been said before, this increase is due to the fact that the densification process intensifies in the materials coded RBD at 1050 ºC because a greater liquid phase is formed, as is shown by the increase in the firing linear shrinkage of these materials at 1050 ºC, which seals the porous originating a decrease in open porosity (Figure 4) and, as a result, an increase of the thermal conductivity.

## 4. Conclusions

According to Braungart and McDonough, [Braungart and McDonough, 2002] authors of the book “Cradle to Cradle,” the products we design must be conceived so that once they have reached the end of their useful life, they can be use as “nutrients” for other processes of the industrial system, that is "technical nutrients” or for nature, "biological nutrients." In this sense and according to the results obtained in this research paper, diatomaceous waste both from vegetable oil filtration industry as well as from the beer brewing industry can be considered technical nutrients when used to manufacture ceramic materials for construction, while dry bending strength values are viable for these mixtures to be introduced in industrial ceramic manufacturing process, such as the manufacturing of bricks

Incorporating both beer and oil diatoms to the manufacturing process of ceramic materials for construction is technically viable as has been shown by the results of the technical characterization of the green and dry materials, the parameters regulating the behavior during the drying process (dry contraction and Nosova index) present improved or optimized values for mixture coded R and so reduce the risk of fissures appearing during the drying process. In addition, the dry bending strength values are adequate for the introduction of these mixtures to the industrial manufacturing process of ceramic materials for construction such as brick manufacturing.

In spite of needing more energy during the drying process given that more water is needed for shaping by extrusion, adding diatomaceous residues reduces energy consumption in the global manufacturing process (drying + firing). This occurs because the energy release during the firing process, due to the combustion of the organic matter present in the residue, is greater than the additional energy needed to dry the shaped material. Additionally, incorporating oil diatoms causes the sintering temperature to be lower, as is shown in the thermal dilatometric analysis, which makes it possible to manufacture ceramic materials for construction sintered at a lower temperature while maintaining the values of the technological properties such as density and strength; however, this fact will have to be corroborated in future research.

Final properties, obtained for the sintered materials containing different quantities of diatomaceous residues, show that all the materials made present bulk density and bending strength values that are within the ranges established for ceramic materials for construction such as bricks; therefore, they are technically viable. These properties are influenced by the porosity developed; hence, when the porosity generated by combustion of the organic material from the residues increases, both the bulk density and bending strength decrease. Furthermore, thermal conductivity also follows and evolution that is inversely proportional to the porosity of the materials.

The decrease originated in the thermal conductivity values of the mixtures that incorporate diatomaceous waste results in obtaining ceramic materials for construction with improved isolating properties that would improve energy efficiency in buildings reducing energy consumption.

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**Table 1:** Chemical analysis of reference clay material and diatomaceous wastes

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | $SO_3$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **R** | 56.1 | 13.0 | 5.0 | - | 2.3 | 7.7 | 0.3 | 3.6 | 0.7 | 0.1 | 0.7 | 10.8 |
| **OD** | 36.1 | 2.4 | 0.9 | 0.1 | 16.2 | 3.1 | 0.1 | 0.6 | 0.1 | 0.2 | 0.1 | 40.0 |
| **BD** | 86.3 | 2.9 | 1.7 | - | 0.2 | 0.8 | 0.3 | 0.5 | 0.5 | 0.5 | 0.1 | 6.0 |

LOI: Loss on Ignition

**Table 2:** Mineralogical analysis of reference clay material and diatomaceous wastes

| | **Q** | **Cr** | **Fd** | **C** | **D** | **SM** | **Ph** | **Phyllosilicates** | | | **Am** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **Es** | **Ill** | **K** | |
| **R** | 40 | n.d. | 7 | 8 | 4 | n.d. | 39 | 29 | 61 | 10 | n.d. |
| **OD** | 5 | n.d. | n.d. | 5 | n.d. | * | n.d. | n.d. | n.d. | n.d. | ** |
| **BD** | 15 | 30 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 55 |

Q: Quartz, Cr: Cristobalite, Fd: Feldspars, C: Calcite, D: Dolomite, SM: MagnesiumSilicate, Ph: Phyllosilicates, Es: Esmectite, Ill: Illite, K: Kaolinite, Am: Amorphous, n.d.: Non detected

* It has not been possible to determine in which phase magnesium is found

** It has not been possible to quantify the amount of amorphous phase. although there is a substantial amount

**Table 3:** Properties of green and dry extruded materials

| | **Working Moisture [%]** | **Dry Linear Shrinkage [%]** | **Nosova Index** | **Dry Bulk Density [g/cm$^3$]** | **Dry Bending Strenght [MPa]** | **Vaporization Energy [Kcal/Kg$_{s\ seco}$]** |
|---|---|---|---|---|---|---|
| **R** | 19.8 ± 0.1 | 5.3 ± 0.1 | 0.68 | 2.02 ± 0.01 | 7.0 ± 0.1 | 106.9 |
| **R3OD** | 20.0 ± 0.1 | 4.8 ± 0.1 | 0.58 | 1.96 ± 0.01 | 7.8 ±0.4 | 108.0 |
| **R7OD** | 19.2 ± 0.1 | 4.6 ± 0.1 | 0.57 | 1.93± 0.01 | 7.7 ±0.4 | 103.7 |
| **R10OD** | 20.4 ± 0.1 | 4.1 ± 0.1 | 0.48 | 1.87 ± 0.01 | 7.3 ±0.7 | 110.2 |
| **R3BD** | 21.2 ± 0.1 | 5.2 ± 0.1 | 0.62 | * | 6.3 ±0.3 | 114.5 |
| **R7BD** | 23.5 ± 0.1 | 5.0 ± 0.1 | 0.53 | * | 5.5 ±0.3 | 126.9 |
| **R10BD** | 21.6 ± 0.1 | 4.6 ± 0.1 | 0.51 | 1.90 ± 0.01 | 5.0 ±0.4 | 116.6 |

* Data not available

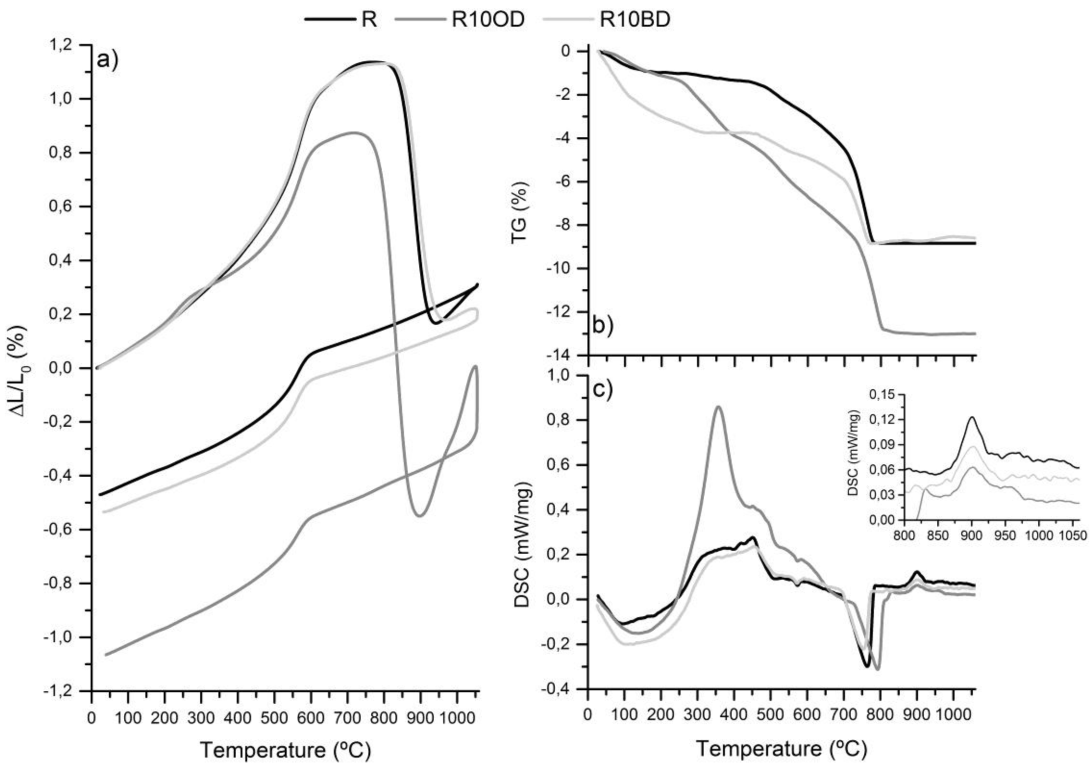

**Figure 1:** Thermal analysis of reference clay material, R, and mixtures incorporating 10% diatomaceous wastes, R10OD and R10BD, up to 1050ºC. a) Thermal dilatometric analysis, b) Thermogravimetric analysis y c) Differential scanning calorimetry.

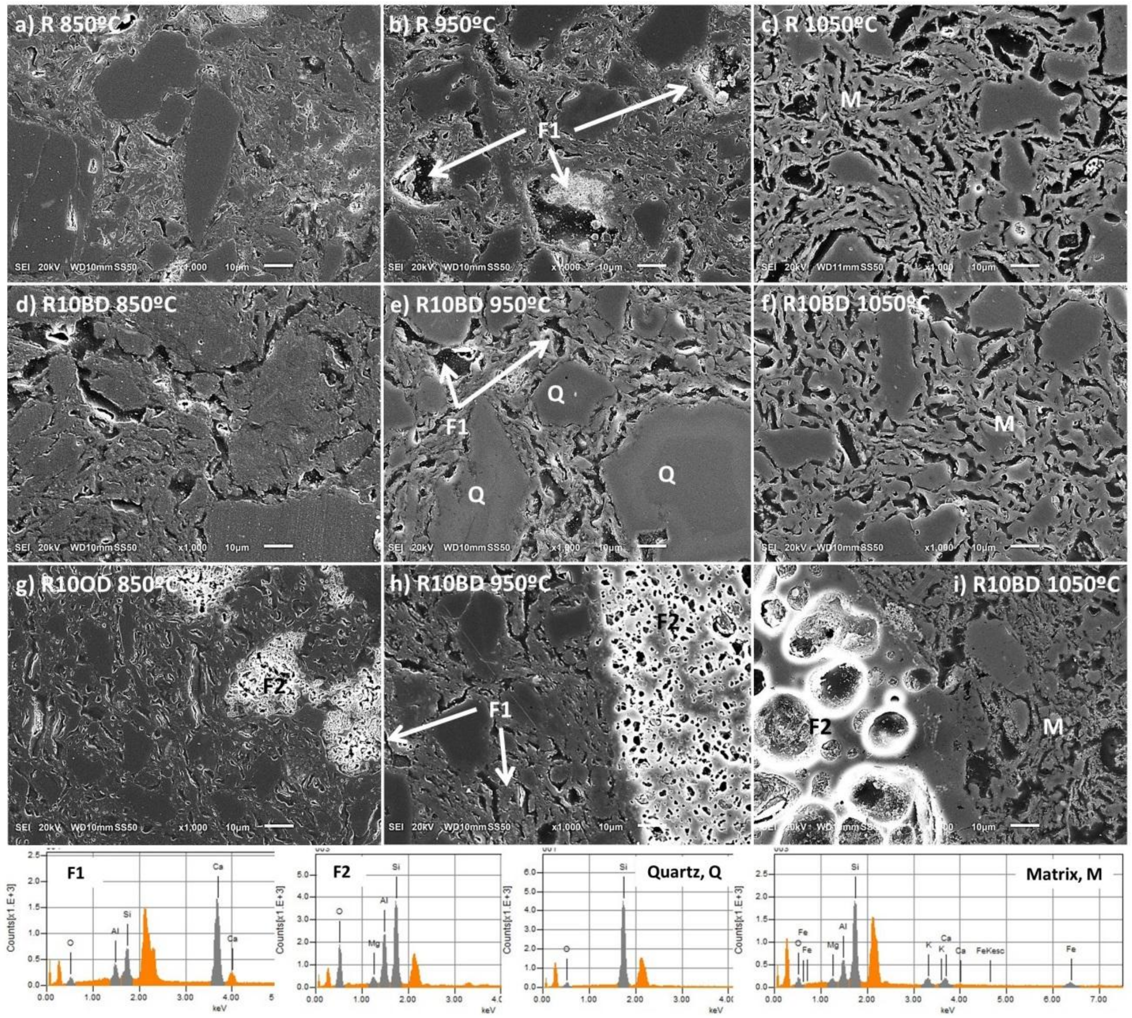

**Figure 1:** SEM images x 1000 increases and EDX analysis of the R, R10BD and R10OD materials to the different sintering temperatures.

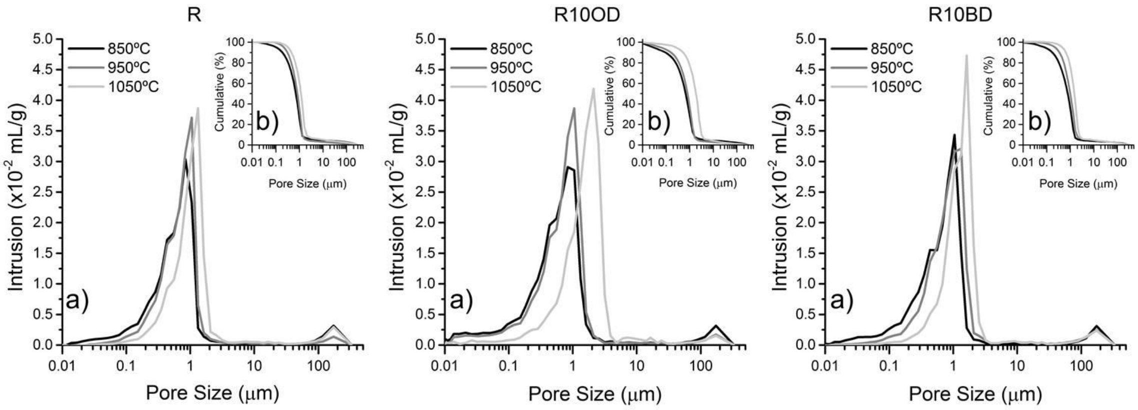

**Figure 1:** Pore Size Distribution of reference clay material, R, and mixtures incorporating 10% diatomaceous wastes, R10OD and R10BD. a) Incremental intrusion and b) cumulative intrusion.

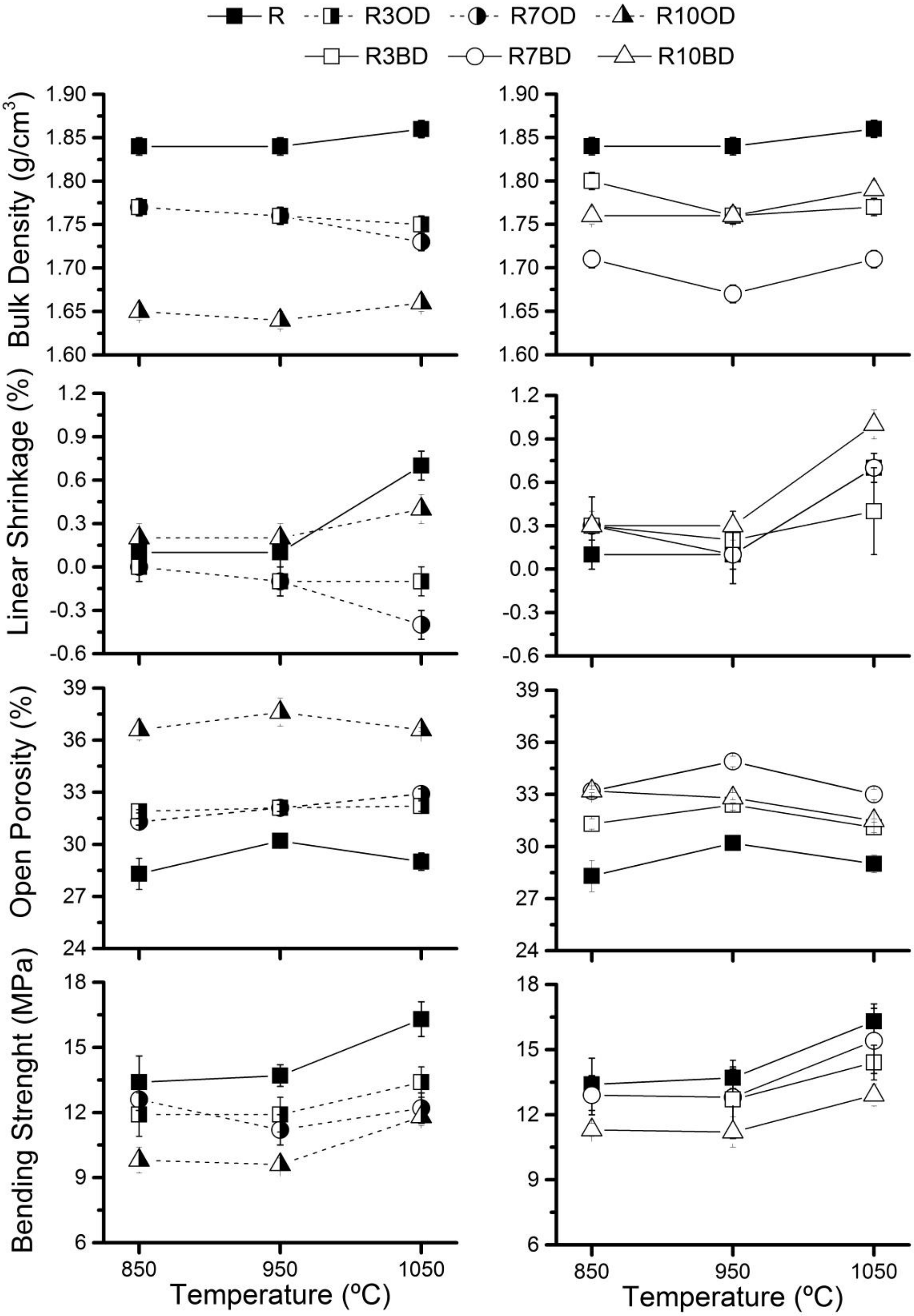

**Figure 1:** Sintering diagram of reference clay material, R, and mixtures incorporating diatomaceous wastes.

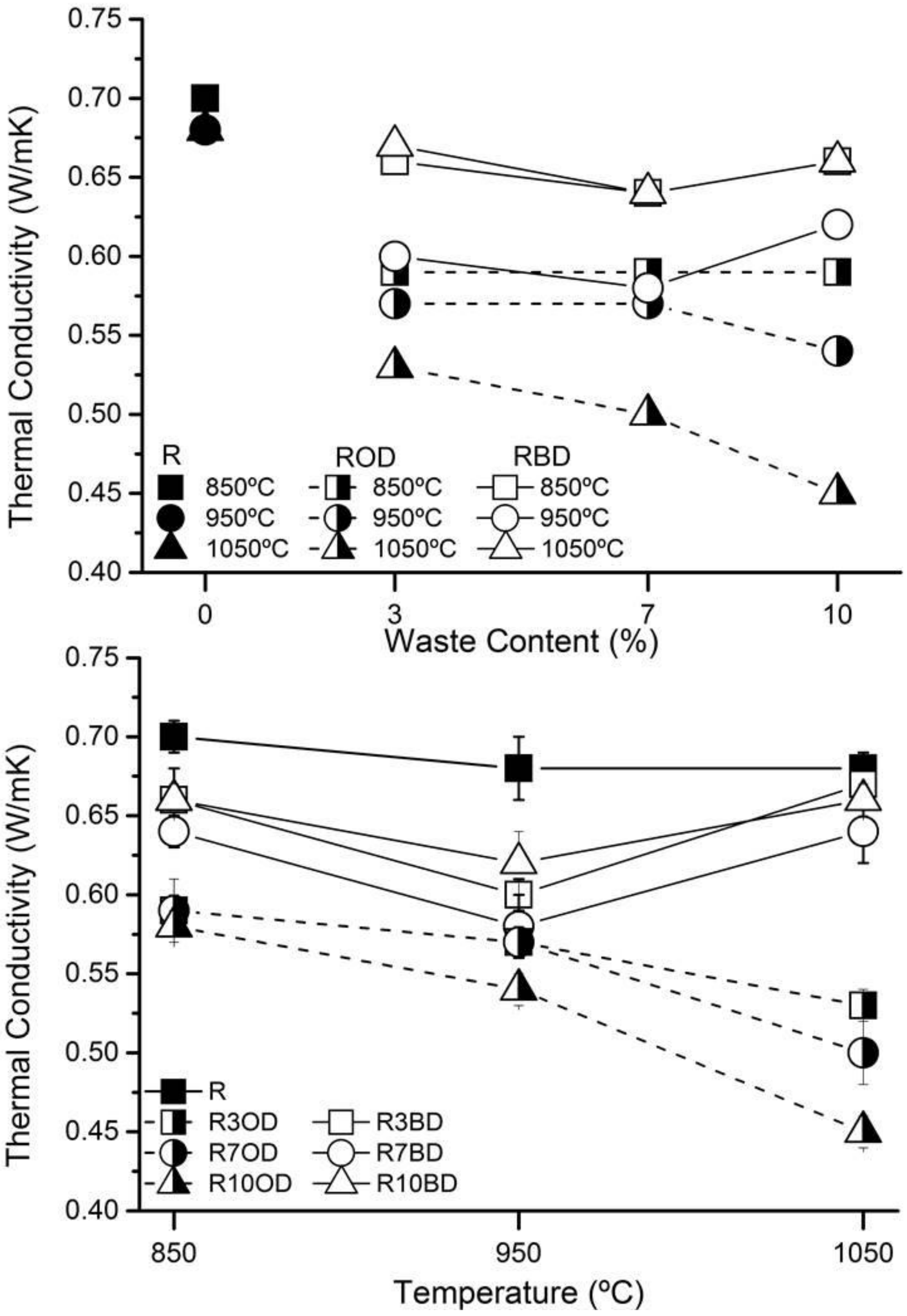

**Figure 5:** Thermal conductivity of materials sintered depending on the a) % wt. of waste, and b) sintering temperature.