Preparation of chamottes as raw material for low-cost ceramic membranes

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PREPARATION OF CHAMOTTES AS RAW MATERIAL FOR LOW-COST CERAMIC MEMBRANES

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Departamento de Ingeniería Química, Instituto Universitario de Tecnología Cerámica, Universitat Jaume I, Castellón, 12006, Spain.

Abstract

Low cost ceramic membranes are usually prepared from a mixture of natural raw materials and some organic porogen agent, as starch. The fact that the porogen must be completely eliminated during firing, leaving an interconnected porous structure, impose large firing times, increasing the final price. A study about the synthesis of porous chamottes as an alternative to organic pore formers was conducted to reduce firing costs. Chamottes were obtained from mixtures of a clay and starch. Different starches were used and the influence of the composition and processing variables were studied. The viability of the porous chamottes was demonstrated.

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1. Introduction

Ceramic membranes are porous materials with controlled porosity and pore size distribution that present several advantages when compared with polymeric membranes, such as thermal, mechanical and chemical resistance\textsuperscript{1,2}. Early work on ceramic membranes were based on raw materials such as alumina, zirconia, titania and silica but the cost of some of these parts was a considerable proportion of the operating cost of processes with ceramic membranes\textsuperscript{3}. In consequence, efforts were made to prepare membranes or supports for membrane layers with low cost or local raw materials. In order to create porosity, gas forming additives or materials that are eliminated during firing are introduced into the raw materials mixture\textsuperscript{4,5}. Among those pore formers there are two widely used, that is, carbonates and starch.

Monash et al.\textsuperscript{2} fabricated a macroporous ceramic support, which presented high permeability and strength, using locally available low-cost raw materials (kaolin, ballclay, feldspar, pyrophyllite and quartz) and calcium carbonate with polyvinyl alcohol as a binder. Emani et al.\textsuperscript{1} prepared ceramic membranes for juice filtration with mixtures of kaolin, quartz and calcium carbonate by uniaxial pressing, following previous research from Nandi\textsuperscript{3} and Vasanth\textsuperscript{6}. Resistant porous membrane supports with porosities ranging between 45 % and 52 % were prepared from an Algerian kaolin and calcite\textsuperscript{7,8} that could be used for different microfiltration and ultrafiltration membranes deposition and could replace the more expensive, commercial alumina supports. Zhou et al.\textsuperscript{9} prepared low cost macroporous supports for ceramic membranes by reaction sintering from local kaolin and dolomite. The porous supports were prepared by extrusion and the final porosity and pore size was determined by the amount of dolomite and the sintering temperature.
In order to decrease the membrane cost by using regional raw materials Almandoz et al. \cite{10} prepared composite ceramic membranes (support and active layer) for application in microfiltration processes. The particle size, composition and sintering temperature of mixtures of clay, quartz, feldspar, alumina, bentonite, magnesium silicate and calcium carbonate were studied. They concluded that porosity depended on sintering temperature while pore size was mainly controlled by the particle size of the starting raw materials mixture. The use of limestone as pore generating material in mixtures of kaolin, feldspars and white clay was evaluated to obtain porous materials for environmental applications \cite{11}. The three compositions tested showed porosity, pore size and permeability values that were sufficient to be used in separation processes.

Starches are widely employed to generate porosity in ceramics as they burn out around 500\textdegree C \cite{12-14}, and can help in the consolidation of ceramic bodies obtained by casting processes \cite{15,16}. Low cost porous support membranes with 38% porosity and acceptable water permeability values \cite{17} were prepared from a mixture of Tunisian clay, kaolin and 9 wt% of corn starch. In order to obtain filters to be used in the wastewater treatment for Moroccan textile industry, membranes were prepared from clays and phosphates coming from Moroccan ores and different contents of starch \cite{18}. Other pore-formers \cite{19} such as sawdust have been mixed with local raw materials to prepare low cost membranes and/or membrane supports \cite{20,21}. However, the use of these pore-formers that burn-out during the sintering of the ceramic membrane implies long firing cycles to prevent breakage and defects, having a negative effect on the processing cost.

Chamottes have been widely used in the ceramic industry to obtain insulating \cite{22} and refractory \cite{23,24} materials as they behave as an inert raw material during the firing cycle and so improve the processing by controlling the shrinkage and porosity of the final
product. In order to obtain low-cost ceramic membranes by minimizing the cost of the firing step, a study was conducted to determine the possibility of preparing porous chamottes to be used in low-cost membrane’s synthesis as an alternative to organic poreforming agents.

2. Experimental Procedure

The clay UA-50 (Mineraria, Spain) was selected to prepare the chamottes as it had been previously used as raw material for low-cost ceramic membranes. The clay composition was approximately 65.6 SiO$_2$, 22.8 Al$_2$O$_3$, 0.6 Na$_2$O, 2.3 K$_2$O, 1.3 TiO$_2$, 1.1 Fe$_2$O$_3$, 0.3 CaO and 0.5 MgO, with a loss on ignition of 6.5 (wt%).

The chamottes were obtained from a mixture of 90 wt% clay and 10 wt% starch, using three different starches: S1 (potato starch, Roquette Freres S.A., France), S2 (pea fiber L50M, Roquette Freres S.A., France) and S3 (soluble potato starch Pregeflo P100, Roquette Freres S.A., France). Besides a reference chamotte, without starch, was also prepared for comparative purposes.

The particle size distribution of the starches was obtained by dry laser diffraction (Mastersizer 2000, Marvern Instruments Ltd. UK) and the characteristic diameter $D_{10}$, $D_{50}$, $D_{90}$, $D_V$ and $D_S$ were calculated (the parameters $D_{90}$, $D_{50}$ and $D_{10}$ are the cut off particle size below which 90 %, 50 % and 10 % of the total particle volume lies and the parameters $D_V$ and $D_S$ are respectively the volume mean diameter and the surface area mean diameter). The humidity was obtained from the weight loss after drying at 110 °C in an electrical oven (it was given as kg of water by 100 kg of dry solid) and the ash content was determined by calcining every starch at 1000 °C.

Several methods were used to prepare clay-starch agglomerates: a dry method (D) and three wet methods (W1, W2 and W3). The dry method (D) consisted in preparing the
mixture in a blade mill (Multitrio, Moulinex International, France) adding the starch gradually to avoid the formation of large agglomerates. Next, granulation was carried out by spraying water onto the powder mixture before introducing it in a homemade granulator. Wet methods consisted in preparing aqueous slurries by dispersion of the clay-starch mixture with a high speed disperser. Slurry solids loading was 50 wt%. The suspensions were spray dried at 200 °C in a laboratory spray dryer (W1 method) if their viscosity was adequate. When the viscosity was too high to be spray dried, the slurries were dried in an oven (W2 method) or under infrared lamps (W3 method). In both methods, W2 and W3, clay-starch agglomerates were obtained by milling the dry mixture in a blade mill and sieving through a 300 µm mesh.

Several chamottes were prepared by adding different amounts of starch, using different preparation methods and firing the clay-starch agglomerates in an electric kiln to peak temperatures from 1050 to 1200°C with a heating rate of 10 °C/min and a soaking time of 1 hour (Table I). Loss of ignition (LOI) was determined after firing to assess the complete oxidation of the starch.

Ceramic membranes were prepared with the chamottes and a mixture of clay UA-50 (Mineraria, Spain), micronized sodium feldspar (courtesy of Pamesa, S.A. Spain) and feldspathic sand (AFS-125, Imerys, Spain) in a weight ratio of 40:40:20, respectively. Different weight percentages of chamotte ranging from 15 to 60 wt% were added to the clay-feldspars mixture (Table II and Table III), whose composition was approximately 72.0 SiO₂, 17.6 Al₂O₃, 4.2 Na₂O, 1.5 K₂O, 0.6 TiO₂, 0.5 Fe₂O₃, 0.3 CaO and 0.2 MgO, with a loss on ignition of 2.9 (wt%).

The membrane compositions were moistened to a water content of 0.055 kg water/dry solid kg and disk-shaped test specimens of 50 mm diameter and 3-4 mm thickness were
formed by uniaxial dry pressing at 300 kg cm$^{-2}$ and dried in an oven at 110°C. Specimen dimensions and bulk density of the green samples, and later of the sintered ones, were then determined by the mercury displacement method.

The green specimens were fired in a fast electric kiln (Pirometrol S.A. Spain) at different peak temperatures, ranging from 1050 to 1125 °C (4 specimens of each composition were tested at every temperature). The heating rate was 25 °C/min, with a 60 min hold at peak temperature. The firing cycle was designed to find a compromise between the amount of porosity and mechanical strength in the sintered membranes.

The pore size distribution of the chamottes and the membranes was measured by mercury intrusion porosimetry$^{26}$ (AutoPore IV 9500, Micromeritics Instruments Co, USA). Sample weight was about 2 g and a 130° contact angle was taken. The pore size distributions were fitted to log-normal distributions and characteristic pore diameters ($d_{16}$, $d_{50}$, and $d_{84}$), were calculated. The values of $d_{16}$ and $d_{84}$ were considered representatives of the coarse and fine pore fraction in the distribution, respectively. The parameter $d_{16}$ corresponds to the diameter above which 16 % of total pore volume is found and $d_{84}$ value corresponds to the diameter above which 84 % of total pore volume is found. Surface area$^{27}$ (BET method: Tristar 3000 Micromeritics) of the chamottes was also determined.

Apparent porosity, measured as water uptake according to standard UNE-EN ISO 10545-3$^{28}$, was also determined and the permeability coefficient for water was obtained with a liquid permeameter (LEP101-A, PMI, USA). Additionally, the microstructure of the chamottes as well as the membranes was examined by FEG-SEM (Quanta 200F, FEI Co, USA).
3. Results and discussion

3.1 Chamotte preparation

The starches’ characteristics are shown in Figure 1 and Table IV. The three starches covered a broad range of particle size, a parameter related with the pore size generated in the final product, as previously shown.\(^2^5\)

Agglomerates of 90 wt% clay + 10 wt% starch were fired to different maximum temperatures from 1050 to 1200 °C. The weight loss (%) was selected to monitor the starch decomposition. Table V shows the results for agglomerates prepared by dry method using the three starches S1, S2 and S3. There is no difference in weight loss for 1100 up to 1200 °C only slight variations that must be due to experimental uncertainty. Differences between series can be explained by the different origins of the starches that confer them different ash content, as it has been shown in Table IV.

To determine the effect of the preparation method and the type of starch used, the mean weight loss of the agglomerates obtained at 1100, 1150 and 1200 °C of peak temperature was determined and plotted for all the prepared series (Figure 2). For purposes of comparison, the data for clay agglomerates, without starch, have also been included.

Spray dried agglomerates (W1 method) could only be obtained with slips prepared with clay and the mixture 90 % clay + 10 % S2, as the other slips were too viscous to be spray dried. Results show that the weight losses are more influenced by the preparation method than by the type of starch used. The fact that wet methods give lower weight losses could be due to a partial dehydration of the starch during drying. In the case of IR drying a partial burning of the starch directly exposed to radiation was visually detected. In consequence, the weight loss tends to be slightly lower.
Weight losses are representative of starch oxidation during firing but a priori have no direct relationship with the porous texture of the chamotte granules. In order to use the chamottes as raw material for membranes they must behave in an inert manner during the firing of the membranes and the degree of sintering must be low enough to avoid the collapse of pores, maintaining a connected open porosity. The sintering process must also confer to the chamotte granules a relatively high mechanical strength to avoid being crushed during the membrane shaping process.

The maximum mechanical strength was assumed to correspond to the chamottes prepared at 1200 °C. So, to evaluate the pore structure of these samples, the chamotte granules obtained at 1200 °C from agglomerates prepared by dry (D) and wet W2 methods were selected. Pore size distribution (PSD) and surface area were determined. The corresponding data are listed in Table VI. Figure 3 plots the pore size distributions of the six chamottes. The curves corresponding to chamottes prepared by dry (D) method have a higher pore volume in the range 2-20 µm, what is quite convenient to obtain an adequate permeability value. Taking into account that the dry method is easier, more reproducible and environmentally friendlier than the wet methods, chamottes D seem to be a good option. Among these, the higher BET area and lower total pore volume obtained by mercury porosimetry of 10S1-D suggest that this chamotte must have a big amount of very small pores, that is, pores not accessible to the mercury during the porosimetry test.

According to the PSD data (Table VI), 10S2-D, 10S3-D and 10S1-W2 chamottes have the highest total pore volume and could be successfully used to prepare membranes. BET area for 10S1-W2 is the highest but, as it has been already mentioned, this is due to a high number of small pores. When pores are taken to be cylinders a pore wall area
can be calculated based on a pore volume (V) and a pore size (d). An equivalent surface area has been calculated by using $d_{84}$ (representative of small pores) and the total pore volume ($V_T$) obtained in mercury porosimetry ($S_{CALC}=4V_T/d_{84}$). On representing $S_{CALC}$ values versus $S_{BET}$ a linear trend can be observed (Figure 4) confirming that small pores are representative of specific surface area.

In order to determine the effect of the starch content on the characteristics of the chamotte, a second series of agglomerates were prepared from mixtures of 70 wt% clay + 30 wt% starch S1, by the D and W2 method. The agglomerates were fired at 1200 °C of maximum temperature. No significant differences were found between the new chamotte granules and the previous ones, obtained with 10 wt% starch S1.

The chamottes consisted of hard porous agglomerates without important differences in microstructure (Figure 5). It seems that some granules have the pore network completely connected with the surface, but others have a more compact crust that partially blocks the connection. It was not possible to measure the proportion of every kind of granule in the chamottes. In consequence, the selection of the optimal chamotte should be addressed after analyzing its effects on the properties of the membranes.

3.2 Chamottes as raw material for membranes

Firing cycles of the membranes were much shorter when chamotte was used instead of starch as pore generator. For the same peak temperature, a membrane prepared by mixing 15 wt% starch with the remaining raw materials must be treated with a firing cycle of 6 hours. On the contrary, when the membrane is prepared by mixing chamotte with the remaining raw materials the firing cycle lasts only 2 hours.
Ceramic membranes prepared with 15 wt% of all the synthesized chamottes had green density values in the range 1.76 to 1.83 g·cm\(^{-3}\), lower than the membrane without chamotte (1.87 g·cm\(^{-3}\)).

Bulk density of the membranes increased with firing temperature (Figure 6) meaning that the maximum densification has not been reached. In general, membranes with chamottes obtained by the wet method W2 give membranes with lower bulk density but there was no clear effect of the type of starch used.

A direct relationship between bulk densities of the membranes obtained with all the chamottes and firing cycles and open porosity, measured as water absorption, was found (Figure 7). These outcomes suggest that there is hardly any difference between using one or other chamotte, and that the firing cycle is the variable that determines the final porosity of the membrane, in the studied range. Nevertheless, the properties that decide whether the membranes are appropriate or not for filtration purposes are the permeability and the mechanical strength.

On comparing membranes obtained with the same firing cycle, no important differences in permeability were found. Even membranes prepared with chamottes from agglomerates with 30 wt% of starch (C1 and A1) had similar permeability values, contrary to what might be expected. If a high percentage of starch is used to prepare chamottes, an important fraction can remain on the surface of the clay-starch agglomerates. This starch will burn during the firing schedule without forming porosity in the chamotte granules.

Permeability values rose with temperature up to a peak value for each membrane’s composition, as Figure 8 shows. This variation is due to densification of the membranes. As firing temperature rose, liquid phase forms and small pores progressively
disappeared, leading to a differential shrinkage in the sample that enlarges the biggest pores and increases permeability. At higher temperatures, when a significant amount of liquid phase forms, the initially interconnected porous system is blocked and permeability decreases. According to those findings the best membranes are those obtained with a peak temperature of 1075 °C.

3.3 Effect of the chamotte content on the membrane’s properties

To study the effect of the chamotte content on the processing and the permeability of the resulting membrane, three series of membranes (A, B and C) were prepared with different chamottes. The selected chamottes were 10S1-W2, 10S3-W2 and 10S1-D. In each series the chamotte percentage ranged from 30 to 60 %wt. Besides, for comparative purposes, another series (R) was also prepared (Table III). The green density values of these membranes are given in Table VII. For each series, green density of the membranes decreased as the chamotte content increased, as a consequence of the mixed contributions of the lower apparent density of chamotte and the lower compaction during pressing. When the results of test pieces from series A, B and C, having the same chamotte content are compared, the pieces made with the 10S1-W2 chamotte are observed to display considerably lower green densities than those prepared with the other two chamottes.

Figure 9 plots the bulk density of the membranes obtained at 1075 and 1100 °C of maximum firing temperature versus green density. As it was expected, there is a direct relationship between green density and bulk density of the membranes. Samples fired at 1075 °C have lower bulk densities than samples fired at 1100 °C. These results are consistent with those obtained for membranes with 15 wt% chamotte (Figure 6) and are a consequence of the pore elimination during sintering. Raising temperature lowers
specimen porosity further until maximum densification is reached. As membranes need to be porous, firing temperature should be as low as possible provided that mechanical strength would be enough to allow operation of the membrane. No problems associated with low mechanical strength were observed and consequently 1075 °C was selected as firing temperature to obtain the membranes.

Figure 10 shows that for each series of membranes obtained at 1075 °C, open porosity, measured as water absorption, increased as chamotte content augments and that the most porous membranes correspond to series A. Water absorption includes pores opened to the surface but not necessarily all the pores measured in water absorption are interconnected in such a way that allows the water flow through the membrane. So, in order to determine the best chamotte to prepare membranes, permeability values have to be addressed.

Figure 11 plots water permeability values of the membranes prepared at 1075 °C to visualize the effect of the chamotte content. The permeability of the R1 membrane was too low to be measured because this membrane did not contain any pore generator. It can be observed that the R2 membrane has the same permeability as the membranes prepared with 15 wt % of chamotte, which reveals the importance of including feldspar and feldspathic sand in the composition. For all the series, permeability increases with chamotte content and for values lower than 45 wt % there are no clear differences among the different chamottes, as all the values are quite similar when chamotte content is the same. However, for membranes with 60 wt% of chamotte the higher permeability corresponds to series A, that is, the membrane prepared with the 10S1-W2 chamotte. The results for membranes fired at 1100 °C showed a similar trend but the permeability values were slightly lower due to the initial formation of closed porosity that decreases
the connectivity of the capillary system. On further increasing the chamotte content the resulting composition had processing problems so the upper limit of 60 wt% was established.

Pore size distribution, porosity and permeability define the performance of the membrane. Mercury porosimetry results (Table VIII) show that membranes prepared with 60 wt% chamotte and fired at 1075 °C have narrow pore size distributions centered around 2µm what makes all of them valuable for infiltration purposes 32, 33.

4. Conclusions

In order to try and avoid burning of organic pore formers during membrane’s processing, porous chamottes were prepared starting from clay and starch agglomerates. Different types and proportions of starch were used. There were no significant differences between chamottes prepared with different starches, but it was observed that the processing method to obtain the clay-starch agglomerates had influence on the porosity of the resulting chamotte. The chamottes consisted of hard porous agglomerates with an interconnected pore network and allow membranes with considerably shorter firing cycles to be made than when starch was used as the pore former.

Membranes were prepared by pressing a mixture of white clay, sodium feldspar, feldspathic sand and different proportions of chamottes and firing at peak temperatures from 1000 to 1200 °C. Permeability values increase with firing temperature up to 1075 °C and then decreased due to the membrane’s densification that reduces the interconnectivity of the pore network. As the membranes had enough mechanical strength, 1075 °C was set as optimum firing temperature of the membranes.
It was shown that the permeability of the membranes increased with chamotte content and for values lower than 45 wt % there were no clear differences among the different chamottes. However, with 60 wt% of chamotte the highest permeability corresponded to the membrane prepared with the 10S1-W2 chamotte. Membranes with more than 60 wt% chamotte could not be obtained due to processing problems so the upper limit of 60 wt% was established. Low cost membranes with narrow pore size distribution centered around 2 µm can be successfully obtained with short firing cycles when porous chamottes are used instead of traditional pore formers.

5. Acknowledgements

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Figure Captions

Figure 1. Starches’ particle size distributions.

Figure 2. Mean weight loss of the agglomerates used to synthesize the chamottes.

Figure 3. Pore size distribution of chamotte granules prepared with S1, S2 and S3 starches by dry (D) (a), and wet (W2) (b) method and fired at 1200 °C.

Figure 4. Equivalent surface area from mercury porosimetry versus BET area values.

Figure 5. Microstructure of the chamottes obtained by firing at 1200 °C agglomerates prepared with starches S1 and S2 by dry (D) and wet W2 method.

Figure 6. Bulk density of the membranes with 15 wt% chamotte.

Figure 7. Open porosity, measured as water absorption, versus bulk density of membranes with 15 wt% of chamotte.

Figure 8. Variation of permeability with firing temperature for membranes prepared with 15 wt% of 10S1-D (C0), 10S2-D (D0) and 10S3-W2 (B0) chamottes.

Figure 9. Bulk density of the membranes fired at 1075 and 1100 °C.

Figure 10. Variation of the open porosity of the membranes fired at 1075 °C with their chamotte content.

Figure 11. Variation of the water permeability of the membranes fired at 1075 °C with their chamotte content.
Tables

Table I. List of prepared chamottes.

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Table II. Composition of the series of membranes prepared (Series 0).

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Table III. Composition of the series of membranes prepared (Series R, A, B and C).

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</tr>
<tr>
<td>Feldespic sand (%wt)</td>
<td>20</td>
<td>-</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Chamotte 10S1-W2 (%wt)</td>
<td>-</td>
<td>60</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>Chamotte 10S3-W2 (%wt)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chamotte 10S1-D (%wt)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table IV. Starches characterization.

<table>
<thead>
<tr>
<th>Reference</th>
<th>D_{10}(µm)</th>
<th>D_{50}(µm)</th>
<th>D_{90}(µm)</th>
<th>D_{v}(µm)</th>
<th>D_{s}(µm)</th>
<th>Moisture (%)</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>26</td>
<td>46</td>
<td>76</td>
<td>49</td>
<td>41</td>
<td>22.3</td>
<td>0.71</td>
</tr>
<tr>
<td>S2</td>
<td>16</td>
<td>75</td>
<td>184</td>
<td>90</td>
<td>35</td>
<td>8.7</td>
<td>3.53</td>
</tr>
<tr>
<td>S3</td>
<td>20</td>
<td>63</td>
<td>136</td>
<td>72</td>
<td>33</td>
<td>4.5</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table V. Effect of the peak temperature on the weight loss of agglomerates prepared by dry method.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10S1-D</td>
</tr>
<tr>
<td>1050</td>
<td>17.23</td>
</tr>
<tr>
<td>1100</td>
<td>18.39</td>
</tr>
<tr>
<td>1150</td>
<td>18.30</td>
</tr>
<tr>
<td>1200</td>
<td>18.18</td>
</tr>
</tbody>
</table>
Table VI. Characteristic pore diameters, total pore volume and BET surface area for chamottes obtained at 1200 ºC from agglomerates prepared with 90 wt% clay + 10 wt% starch.

<table>
<thead>
<tr>
<th>Chamotte</th>
<th>S_{BET} (m²·g⁻¹)</th>
<th>d_{16} (µm)</th>
<th>d_{50} (µm)</th>
<th>d_{84} (µm)</th>
<th>Total pore volume V₁ (cm³·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10S1-D</td>
<td>0.43</td>
<td>21.75</td>
<td>9.10</td>
<td>2.88</td>
<td>0.641</td>
</tr>
<tr>
<td>10S2-D</td>
<td>0.31</td>
<td>23.74</td>
<td>12.85</td>
<td>6.28</td>
<td>0.779</td>
</tr>
<tr>
<td>10S3-D</td>
<td>0.37</td>
<td>31.94</td>
<td>13.53</td>
<td>3.60</td>
<td>0.769</td>
</tr>
<tr>
<td>10S1-W2</td>
<td>0.59</td>
<td>31.83</td>
<td>7.66</td>
<td>2.25</td>
<td>0.714</td>
</tr>
<tr>
<td>10S2-W2</td>
<td>0.50</td>
<td>22.55</td>
<td>8.48</td>
<td>2.88</td>
<td>0.674</td>
</tr>
<tr>
<td>10S3-W2</td>
<td>0.16</td>
<td>30.01</td>
<td>18.32</td>
<td>8.38</td>
<td>0.554</td>
</tr>
</tbody>
</table>

Table VII. Green densities of the four series of membranes prepared.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>R1</th>
<th>R2</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green density (g·cm⁻³)</td>
<td>1.87</td>
<td>1.59</td>
<td>1.67</td>
<td>1.55</td>
<td>1.48</td>
<td>1.81</td>
<td>1.75</td>
<td>1.70</td>
<td>1.70</td>
<td>1.55</td>
<td></td>
</tr>
</tbody>
</table>

Table VIII. Characteristic pore diameters, total pore volume, water permeability and open porosity for membranes with 60 wt% of chamotte (Sintering temperature 1075 ºC).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>d_{16} (µm)</th>
<th>d_{50} (µm)</th>
<th>d_{84} (µm)</th>
<th>Total pore volume (cm³·g⁻¹)</th>
<th>Water permeability (L·h⁻¹·m⁻²·bar⁻¹)</th>
<th>Open porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>2.37</td>
<td>1.85</td>
<td>1.17</td>
<td>0.213</td>
<td>1390</td>
<td>35</td>
</tr>
<tr>
<td>B3</td>
<td>3.01</td>
<td>2.25</td>
<td>1.21</td>
<td>0.140</td>
<td>1190</td>
<td>26</td>
</tr>
<tr>
<td>C3</td>
<td>1.89</td>
<td>1.52</td>
<td>0.92</td>
<td>0.177</td>
<td>920</td>
<td>31</td>
</tr>
</tbody>
</table>
Figure 1. Starches’ particle size distributions.

Figure 1
57x64mm (600 x 600 DPI)
Figure 2. Mean weight loss of the agglomerates used to synthesize the chamottes.
Figure 3. Pore size distribution of chamotte granules prepared with S1, S2 and S3 starches by dry (D) (a), and wet (W2) (b) method and fired at 1200 °C.

Figure 3
57x32mm (600 x 600 DPI)
Figure 4. Equivalent surface area from mercury porosimetry versus BET area values.

\[ R^2 = 0.930 \]

\[ S_{\text{CALC}} \text{ (m}^2\cdot\text{g}^{-1}) \]

\[ S_{\text{BET}} \text{ (m}^2\cdot\text{g}^{-1}) \]

61x74mm (600 x 600 DPI)
Figure 5. Microstructure of the chamottes obtained by firing at 1200 °C agglomerates prepared with starches S1 and S2 by dry (D) and wet W2 method.
Figure 6. Bulk density of the membranes with 15 wt% chamotte.
Figure 7. Open porosity, measured as water absorption, versus bulk density of membranes with 15 wt% of chamotte.

Figure 7

$R^2 = 0.997$
Figure 8. Variation of permeability with firing temperature for membranes prepared with 15 wt% of 10S1-D (C0), 10S2-D (D0) and 10S3-W2 (B0) chamottes.
Figure 9. Bulk density of the membranes fired at 1075 and 1100 °C.
Figure 10. Variation of the open porosity of the membranes fired at 1075 °C with their chamotte content.

Figure 10
62x77mm (600 x 600 DPI)
Figure 11. Variation of the water permeability of the membranes fired at 1075 °C with their chamotte content.

Figure 11

60x71mm (600 x 600 DPI)