

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

Journal:	<i>International Journal of Applied Ceramic Technology</i>
Manuscript ID	ACT-3759.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Lorente-Ayza, M-Magdalena; Instituto Universitario Tecnología Cerámica. Universitat Jaume I, Chemical Engineering Orts, M-Jose; Instituto Universitario Tecnología Cerámica. Universitat Jaume I, Chemical Engineering Gozalbo, Ana; Instituto Universitario Tecnología Cerámica. Universitat Jaume I, Chemical Engineering Mestre, Sergio; Instituto Universitario Tecnología Cerámica. Universitat Jaume I, Chemical Engineering
Keywords:	membranes, permeability, pores/porosity, porous materials

SCHOLARONE™
 Manuscripts

Review

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

M-MAGDALENA LORENTE-AYZA*¹; MARIA-JOSE ORTS; ANA GOZALBO;
SERGIO MESTRE.

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.

Supported by the Spanish Ministerio de Economía y Competitividad (Plan Nacional de I+D, ref. CTQ2012-37450-C02-02).

* magda.lorente@itc.uji.es

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^{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 membranes³. 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^{4,5}. Among those pore formers there are two widely used, that is, carbonates and starch.

Monash et al.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.¹ prepared ceramic membranes for juice filtration with mixtures of kaolin, quartz and calcium carbonate by uniaxial pressing, following previous research from Nandi³ and Vasanth⁶. Resistant porous membrane supports with porosities ranging between 45 % and 52 % were prepared from an Algerian kaolin and calcite^{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.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.

1
2
3
4 In order to decrease the membrane cost by using regional raw materials Almandoz et al.
5
6 ¹⁰ prepared composite ceramic membranes (support and active layer) for application in
7
8 microfiltration processes. The particle size, composition and sintering temperature of
9
10 mixtures of clay, quartz, feldspar, alumina, bentonite, magnesium silicate and calcium
11
12 carbonate were studied. They concluded that porosity depended on sintering
13
14 temperature while pore size was mainly controlled by the particle size of the starting
15
16 raw materials mixture. The use of limestone as pore generating material in mixtures of
17
18 kaolin, feldspars and white clay was evaluated to obtain porous materials for
19
20 environmental applications ¹¹. The three compositions tested showed porosity, pore size
21
22 and permeability values that were sufficient to be used in separation processes.
23
24
25 Starches are widely employed to generate porosity in ceramics as they burn out around
26
27 500°C ¹²⁻¹⁴, and can help in the consolidation of ceramic bodies obtained by casting
28
29 processes ^{15, 16}. Low cost porous support membranes with 38% porosity and acceptable
30
31 water permeability values ¹⁷ were prepared from a mixture of Tunisian clay, kaolin and
32
33 9 wt% of corn starch. In order to obtain filters to be used in the wastewater treatment for
34
35 Moroccan textile industry, membranes were prepared from clays and phosphates
36
37 coming from Moroccan ores and different contents of starch ¹⁸. Other pore-formers ¹⁹
38
39 such as sawdust have been mixed with local raw materials to prepare low cost
40
41 membranes and/or membrane supports ^{20, 21}. However, the use of these pore-formers
42
43 that burn-out during the sintering of the ceramic membrane implies long firing cycles to
44
45 prevent breakage and defects, having a negative effect on the processing cost.
46
47
48 Chamottes have been widely used in the ceramic industry to obtain insulating ²² and
49
50 refractory ^{23, 24} materials as they behave as an inert raw material during the firing cycle
51
52 and so improve the processing by controlling the shrinkage and porosity of the final
53
54
55
56
57
58
59
60

1
2
3
4 product. In order to obtain low-cost ceramic membranes by minimizing the cost of the
5 firing step a study was conducted to determine the possibility of preparing porous
6 chamottes to be used in low-cost membrane's synthesis as an alternative to organic
7 poreforming agents.
8
9
10
11

12 **2. Experimental Procedure**

13
14
15
16 The clay UA-50 (Mineraria, Spain) was selected to prepare the chamottes as it had been
17 previously used as raw material for low-cost ceramic membranes²⁵. The clay
18 composition was approximately 65.6 SiO₂, 22.8 Al₂O₃, 0.6 Na₂O, 2.3 K₂O, 1.3 TiO₂,
19 1.1 Fe₂O₃, 0.3 CaO and 0.5 MgO, with a loss on ignition of 6.5 (wt%).
20
21
22
23

24 The chamottes were obtained from a mixture of 90 wt% clay and 10 wt% starch, using
25 three different starches: S1 (potato starch, Roquette Freres S.A., France), S2 (pea fiber
26 L50M, Roquette Freres S.A., France) and S3 (soluble potato starch Pregeflo P100,
27 Roquette Freres S.A., France). Besides a reference chamotte, without starch, was also
28 prepared for comparative purposes.
29
30
31
32
33
34

35 The particle size distribution of the starches was obtained by dry laser diffraction
36 (Mastersizer 2000, Marvern Instruments Ltd. UK) and the characteristic diameter D₁₀,
37 D₅₀, D₉₀, D_V and D_S were calculated (the parameters D₉₀, D₅₀ and D₁₀ are the cut off
38 particle size below which 90 %, 50 % and 10 % of the total particle volume lies and the
39 parameters D_V and D_S are respectively the volume mean diameter and the surface area
40 mean diameter). The humidity was obtained from the weight loss after drying at 110 °C
41 in an electrical oven (it was given as kg of water by 100 kg of dry solid) and the ash
42 content was determined by calcining every starch at 1000 °C.
43
44
45
46
47
48
49
50
51
52

53 Several methods were used to prepare clay-starch agglomerates: a dry method (D) and
54 three wet methods (W1, W2 and W3). The dry method (D) consisted in preparing the
55
56
57
58
59
60

1
2
3
4 mixture in a blade mill (Multitrio, Moulinex International, France) adding the starch
5
6 gradually to avoid the formation of large agglomerates. Next, granulation was carried
7
8 out by spraying water onto the powder mixture before introducing it in a homemade
9
10 granulator. Wet methods consisted in preparing aqueous slurries by dispersion of the
11
12 clay-starch mixture with a high speed disperser. Slurry solids loading was 50 wt%. The
13
14 suspensions were spray dried at 200 °C in a laboratory spray dryer (W1 method) if their
15
16 viscosity was adequate. When the viscosity was too high to be spray dried, the slurries
17
18 were dried in an oven (W2 method) or under infrared lamps (W3 method). In both
19
20 methods, W2 and W3, clay-starch agglomerates were obtained by milling the dry
21
22 mixture in a blade mill and sieving through a 300 µm mesh.
23
24

25
26 Several chamottes were prepared by adding different amounts of starch, using different
27
28 preparation methods and firing the clay-starch agglomerates in an electric kiln to peak
29
30 temperatures from 1050 to 1200°C with a heating rate of 10 °C/min and a soaking time
31
32 of 1 hour (Table I Table). Loss of ignition (LOI) was determined after firing to assess
33
34 the complete oxidation of the starch.
35
36

37
38 Ceramic membranes were prepared with the chamottes and a mixture of clay UA-50
39
40 (Mineraria, Spain), micronized sodium feldspar (courtesy of Pamesa, S.A. Spain) and
41
42 **feldspathic** sand (AFS-125, Imerys, Spain) in a weight ratio of 40:40:20, respectively²⁵.
43

44
45 Different weight percentages of chamotte ranging from 15 to 60 wt% were added to the
46
47 clay-feldspars mixture (Table II and Table III), whose composition was approximately
48
49 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,
50
51 with a loss on ignition of 2.9 (wt%).
52

53
54 The membrane compositions were moistened to a water content of 0.055 kg water/dry
55
56 solid kg and disk-shaped test specimens of 50 mm diameter and 3-4 mm thickness were
57
58
59
60

1
2
3
4 formed by uniaxial dry pressing at 300 kg cm^{-2} and dried in an oven at 110°C . Specimen
5
6 dimensions and bulk density of the green samples, and later of the sintered ones, were
7
8 then determined by the mercury displacement method.
9

10 The green specimens were fired in a fast electric kiln (Pirometrol S.A. Spain) at
11
12 different peak temperatures, ranging from 1050 to 1125°C (4 specimens of each
13
14 composition were tested at every temperature). The heating rate was $25^\circ\text{C}/\text{min}$, with a
15
16 60 min hold at peak temperature. The firing cycle was designed to find a compromise
17
18 between the amount of porosity and mechanical strength in the sintered membranes.
19

20 The pore size distribution of the chamottes and the membranes was measured by
21
22 mercury intrusion porosimetry ²⁶ (AutoPore IV 9500, Micromeritics Instruments Co,
23
24 USA). Sample weight was about 2 g and a 130° contact angle was taken. The pore size
25
26 distributions were fitted to log-normal distributions and characteristic pore diameters
27
28 (d_{16} , d_{50} , and d_{84}), were calculated. The values of d_{16} and d_{84} were considered
29
30 representatives of the coarse and fine pore fraction in the distribution, respectively. The
31
32 parameter d_{16} corresponds to the diameter above which 16% of total pore volume is
33
34 found and d_{84} value corresponds to the diameter above which 84% of total pore volume
35
36 is found. Surface area ²⁷ (BET method: Tristar 3000 Micromeritics) of the chamottes
37
38 was also determined.
39

40 Apparent porosity, measured as water uptake according to standard UNE-EN ISO
41
42 $10545-3$ ²⁸, was also determined and the permeability coefficient for water was obtained
43
44 with a liquid permeameter (LEP101-A, PMI, USA). Additionally, the microstructure of
45
46 the chamottes as well as the membranes was examined by FEG-SEM (Quanta 200F,
47
48 FEI Co, USA).
49
50
51
52
53
54
55
56
57
58
59
60

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 shown²⁵.

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.

1
2
3
4 Weight losses are representative of starch oxidation during firing but a priori have no
5
6 direct relationship with the porous texture of the chamotte granules. In order to use the
7
8 chamottes as raw material for membranes they must behave in an inert manner during
9
10 the firing of the membranes and the degree of sintering must be low enough to avoid the
11
12 collapse of pores, maintaining a connected open porosity. The sintering process must
13
14 also confer to the chamotte granules a relatively high mechanical strength to avoid
15
16 being crushed during the membrane shaping process.
17

18
19 The maximum mechanical strength was assumed to correspond to the chamottes
20
21 prepared at 1200 °C. So, to evaluate the pore structure of these samples, the chamotte
22
23 granules obtained at 1200 °C from agglomerates prepared by dry (D) and wet W2
24
25 methods were selected. Pore size distribution (PSD) and surface area were determined.
26
27 The corresponding data are listed in Table VI. Figure 3 plots the pore size distributions
28
29 of the six chamottes. The curves corresponding to chamottes prepared by dry (D)
30
31 method have a higher pore volume in the range 2-20 μm, what is quite convenient to
32
33 obtain an adequate permeability value. Taking into account that the dry method is
34
35 easier, more reproducible and environmentally friendlier than the wet methods,
36
37 chamottes D seem to be a good option. Among these, the higher BET area and lower
38
39 total pore volume obtained by mercury porosimetry of 10S1-D suggest that this
40
41 chamotte must have a big amount of very small pores, that is, pores not accessible to the
42
43 mercury during the porosimetry test.
44
45
46
47

48 According to the PSD data (Table VI), 10S2-D, 10S3-D and 10S1-W2 chamottes have
49
50 the highest total pore volume and could be successfully used to prepare membranes.

51
52 BET area for 10S1-W2 is the highest but, as it has been already mentioned, this is due
53
54 to a high number of small pores. When pores are taken to be cylinders a pore wall area
55
56
57
58
59
60

1
2
3
4 can be calculated ²⁹ based on a pore volume (V) and a pore size (d). An equivalent
5
6 surface area has been calculated by using d_{84} (representative of small pores) and the
7
8 total pore volume (V_T) obtained in mercury porosimetry ($S_{CALC}=4V_T/d_{84}$). On
9
10 representing S_{CALC} values versus S_{BET} a linear trend can be observed (Figure 4)
11
12 confirming that small pores are representative of specific surface area.
13
14

15 In order to determine the effect of the starch content on the characteristics of the
16
17 chamotte, a second series of agglomerates were prepared from mixtures of 70 wt% clay
18
19 + 30 wt% starch S1, by the D and W2 method. The agglomerates were fired at 1200 °C
20
21 of maximum temperature. No significant differences were found between the new
22
23 chamotte granules and the previous ones, obtained with 10 wt% starch S1.
24
25

26 The chamottes consisted of hard porous agglomerates without important differences in
27
28 microstructure (Figure 5). It seems that some granules have the pore network
29
30 completely connected with the surface, but others have a more compact crust that
31
32 partially blocks the connection. It was not possible to measure the proportion of every
33
34 kind of granule in the chamottes. In consequence, the selection of the optimal chamotte
35
36 should be addressed after analyzing its effects on the properties of the membranes.
37
38

39 **3.2 Chamottes as raw material for membranes**

40
41
42 Firing cycles of the membranes were much shorter when chamotte was used instead of
43
44 starch as pore generator. For the same peak temperature, a membrane prepared by
45
46 mixing 15 wt% starch with the remaining raw materials must be treated with a firing
47
48 cycle of 6 hours. On the contrary, when the membrane is prepared by mixing chamotte
49
50 with the remaining raw materials the firing cycle lasts only 2 hours.
51
52
53
54
55
56
57
58
59
60

1
2
3
4 Ceramic membranes prepared with 15 wt% of all the synthesized chamottes had green
5
6 density values in the range 1.76 to 1.83 g·cm⁻³, lower than the membrane without
7
8 chamotte (1.87 g·cm⁻³).
9

10 Bulk density of the membranes increased with firing temperature (Figure 6) meaning
11
12 that the maximum densification has not been reached. In general, membranes with
13
14 chamottes obtained by the wet method W2 give membranes with lower bulk density but
15
16 there was no clear effect of the type of starch used.
17

18
19 A direct relationship between bulk densities of the membranes obtained with all the
20
21 chamottes and firing cycles and open porosity, measured as water absorption, was found
22
23 (Figure 7). These outcomes suggest that there is hardly any difference between using
24
25 one or other chamotte, and that the firing cycle is the variable that determines the final
26
27 porosity of the membrane, in the studied range. Nevertheless, the properties that decide
28
29 whether the membranes are appropriate or not for filtration purposes are the
30
31 permeability and the mechanical strength.
32
33

34
35 On comparing membranes obtained with the same firing cycle, no important differences
36
37 in permeability were found. Even membranes prepared with chamottes from
38
39 agglomerates with 30 wt% of starch (C1 and A1) had similar permeability values,
40
41 contrary to what might be expected. If a high percentage of starch is used to prepare
42
43 chamottes, an important fraction can remain on the surface of the clay-starch
44
45 agglomerates. This starch will burn during the firing schedule without forming porosity
46
47 in the chamotte granules.
48
49

50 Permeability values rose with temperature up to a peak value for each membrane's
51
52 composition, as Figure 8 shows. This variation is due to densification of the membranes
53
54
55³⁰. As firing temperature rose, liquid phase forms and small pores progressively
56
57
58
59
60

1
2
3
4 disappeared, leading to a differential shrinkage in the sample that enlarges the biggest
5 pores and **increases** permeability. At higher temperatures, when a significant amount of
6 liquid phase forms, the initially interconnected porous system is blocked and
7 permeability decreases. According to those findings the best membranes are those
8 obtained with a peak temperature of 1075 °C.
9

15 **3.3 Effect of the chamotte content on the membrane's properties**

16
17 To study the effect of the chamotte content on the processing and the permeability of
18 the resulting membrane, three series of membranes (A, B and C) were prepared with
19 different chamottes. The selected chamottes were 10S1-W2, 10S3-W2 and 10S1-D. In
20 each series the chamotte percentage ranged from 30 to 60 %wt. Besides, for
21 comparative purposes, another series (R) was also prepared (Table III). The green
22 density values of these membranes are **given** in Table VII. For each series, green density
23 of the membranes decreased as the chamotte content increased, as a consequence of the
24 mixed contributions of the lower apparent density of chamotte and the lower
25 compaction during pressing. When the results of test pieces from series A, B and C,
26 having the same chamotte content are compared, the pieces made with the 10S1-W2
27 chamotte are observed to display considerably lower green densities than those prepared
28 with the other two chamottes.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43

44 Figure 9 plots the bulk density of the membranes obtained at 1075 and 1100 °C of
45 maximum firing temperature versus green density. As it was expected, there is a direct
46 relationship between green density and bulk density of the membranes. Samples fired at
47 1075 °C have lower bulk densities than samples fired at 1100 °C. These results are
48 consistent with **those** obtained for membranes with 15 wt% chamotte (Figure 6) and are
49 **a** consequence of the pore elimination during sintering³¹. Raising temperature lowers
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 specimen porosity further until maximum densification is reached. As membranes need
5
6 to be porous, firing temperature should be as low as possible provided that mechanical
7
8 strength would be enough to allow operation of the membrane. No problems associated
9
10 with low mechanical strength were observed and consequently 1075 °C was selected as
11
12 firing temperature to obtain the membranes.

13
14 Figure 10 shows that for each series of membranes obtained at 1075 °C, open porosity,
15
16 measured as water absorption, increased as chamotte content augments and that the
17
18 most porous membranes correspond to series A. Water absorption includes pores
19
20 opened to the surface but not necessarily all the pores measured in water absorption are
21
22 interconnected in such a way that allows the water flow through the membrane. So, in
23
24 order to determine the best chamotte to prepare membranes, permeability values have to
25
26 be addressed.
27
28

29
30 Figure 11 plots water permeability values of the membranes prepared at 1075 °C to
31
32 visualize the effect of the chamotte content. The permeability of the R1 membrane was
33
34 too low to be measured because this membrane did not contain any pore generator. It
35
36 can be observed that the R2 membrane has the same permeability as the membranes
37
38 prepared with 15 wt % of chamotte, which reveals the importance of including feldspar
39
40 and feldspathic sand in the composition. For all the series, permeability increases with
41
42 chamotte content and for values lower than 45 wt % there are no clear differences
43
44 among the different chamottes, as all the values are quite similar when chamotte content
45
46 is the same. However, for membranes with 60 wt% of chamotte the higher permeability
47
48 corresponds to series A, that is, the membrane prepared with the 10S1-W2 chamotte.
49
50 The results for membranes fired at 1100 °C showed a similar trend but the permeability
51
52 values were slightly lower due to the initial formation of closed porosity that decreases
53
54
55
56
57
58
59
60

1
2
3
4 the connectivity of the capillary system. On further increasing the chamotte content the
5
6 resulting composition had processing problems so the upper limit of 60 wt% was
7
8 established.
9

10 Pore size distribution, porosity and permeability define the performance of the
11
12 membrane. Mercury porosimetry results (Table VIII) show that membranes prepared
13
14 with 60 wt% chamotte and fired at 1075 °C have narrow pore size distributions centered
15
16 around 2µm what makes all of them valuable for infiltration purposes ^{32, 33}.
17
18

19 20 **4. Conclusions**

21
22 In order to try and avoid burning of organic pore formers during membrane's
23
24 processing, porous chamottes were prepared starting from clay and starch agglomerates.
25
26 Different types and proportions of starch were used. There were no significant
27
28 differences between chamottes prepared with different starches, but it was observed that
29
30 the processing method to obtain the clay-starch agglomerates had influence on the
31
32 porosity of the resulting chamotte. The chamottes consisted of hard porous
33
34 agglomerates with an interconnected pore network and allow membranes with
35
36 considerably shorter firing cycles to be made than when starch was used as the pore
37
38 former.
39
40

41
42 Membranes were prepared by pressing a mixture of white clay, sodium feldspar,
43
44 feldspathic sand and different proportions of chamottes and firing at peak temperatures
45
46 from 1000 to 1200 °C. Permeability values increase with firing temperature up to 1075
47
48 °C and then decreased due to the membrane's densification that reduces the
49
50 interconnectivity of the pore network. As the membranes had enough mechanical
51
52 strength, 1075 °C was set as optimum firing temperature of the membranes.
53
54
55
56
57
58
59
60

1
2
3
4 It was shown that the permeability of the membranes increased with chamotte content
5
6 and for values lower than 45 wt % there were no clear differences among the different
7
8 chamottes. However, with 60 wt% of chamotte the highest permeability corresponded to
9
10 the membrane prepared with the 10S1-W2 chamotte. Membranes with more than 60
11
12 wt% chamotte could not be obtained due to processing problems so the upper limit of
13
14 60 wt% was established. Low cost membranes with narrow pore size distribution
15
16 centered around 2 μm can be successfully obtained with short firing cycles when porous
17
18 chamottes are used instead of traditional pore formers.
19
20

21 22 **5. Acknowledgements**

23
24 The authors wish to thank the student Thibaud Besnard from the Ecole Nationale
25
26 Supérieure d'Ingénieurs de Limoges (France) for his helpful aid during the execution of
27
28 the present work.
29
30

31 32 **6. References**

- 33
34
35 ¹ S. Emani, R. Uppaluri, and M.K. Purkait, "Preparation and characterization of
36
37 low cost ceramic membranes for mosambi juice clarification," *Desalination*, **317**
38
39 32–40 (2013).
40
41 ² P. Monash and G. Pugazhenti, "Development of Ceramic Supports Derived
42
43 from Low-Cost Raw Materials for Membrane Applications and its Optimization
44
45 Based on Sintering Temperature," *Int. J. Appl. Ceram. Technol.*, **8** [1] 227–238
46
47 (2011).
48
49 ³ B.K. Nandi, R. Uppaluri, and M.K. Purkait, "Preparation and characterization of
50
51 low cost ceramic membranes for micro-filtration applications," *Appl. Clay Sci.*,
52
53 **42** [1-2] 102–110 (2008).
54
55 ⁴ Y.I. Komolikov and L.A. Blaginia, "Technology of ceramic micro and
56
57
58
59
60

- 1
2
3
4 ultrafiltration membranes. Review,” *Refract. Ind. Ceram.*, **43** [5-6] 181–187
5
6 (2002).
7
- 8 5 S. Gupta and M.F. Riyad, “Oxidation-induced sintering: An innovative method
9
10 for manufacturing porous ceramics,” *Int. J. Appl. Ceram. Technol.*, **11** [5] 817–
11
12 823 (2014).
13
- 14 6 D. Vasanth, R. Uppaluri, and G. Pugazhenti, “Influence of Sintering
15
16 Temperature on the Properties of Porous Ceramic Support Prepared by Uniaxial
17
18 Dry Compaction Method Using Low-Cost Raw Materials for Membrane
19
20 Applications,” *Sep. Sci. Technol.*, **46** [8] 1241–1249 (2011).
21
22
- 23 7 A. Harabi, F. Zenikheri, B. Boudaira, F. Bouzerara, A. Guechi, and L. Foughali,
24
25 “A new and economic approach to fabricate resistant porous membrane supports
26
27 using kaolin and CaCO₃,” *J. Eur. Ceram. Soc.*, **34** [5] 1329–1340 (2014).
28
29
- 30 8 A. Harabi, A. Guechi, and S. Condom, “Production of Supports and Filtration
31
32 Membranes from Algerian Kaolin and Limestone,” *Procedia Eng.*, **33** [2011]
33
34 220–224 (2012).
35
36
- 37 9 J. Zhou, X. Zhang, Y. Wang, A. Larbot, and X. Hu, “Elaboration and
38
39 characterization of tubular macroporous ceramic support for membranes from
40
41 kaolin and dolomite,” *J. Porous Mater.*, **17** [1] 1–9 (2010).
42
43
- 44 10 M. Almandoz, C.L. Pagliero, N.A. Ochoa, and J. Marchese, “Composite ceramic
45
46 membranes from natural aluminosilicates for microfiltration applications,”
47
48 *Ceram. Int.*, **41** [4] 5621–5633 (2015).
49
- 50 11 L. Simão, R.F. Caldato, M.D.M. Innocentini, and O.R.K. Montedo,
51
52 “Permeability of porous ceramic based on calcium carbonate as pore generating
53
54 agent,” *Ceram. Int.*, **41** [3] 4782–4788 (2015).
55
56
57
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- 12 G.C.C. Yang and C.-M. Tsai, "Effects of starch addition on characteristics of tubular porous ceramic membrane substrates," *Desalination*, **233** [1-3] 129–136 (2008).
- 13 S. Li, C.-A. Wang, and J. Zhou, "Effect of starch addition on microstructure and properties of highly porous alumina ceramics," *Ceram. Int.*, **39** [8] 8833–8839 (2013).
- 14 T. Wan, D. Yao, J. Yin, Y. Xia, K. Zuo, and Y. Zeng, "The Microstructure and Mechanical Properties of Porous Silicon Nitride Ceramics Prepared via Novel Aqueous Gelcasting," *Int. J. Appl. Ceram. Technol.*, **12** [5] 932–938 (2015).
- 15 E. Gregorová, W. Pabst, and I. Boháčenko, "Characterization of different starch types for their application in ceramic processing," *J. Eur. Ceram. Soc.*, **26** [8] 1301–1309 (2006).
- 16 E. Gregorová and W. Pabst, "Porosity and pore size control in starch consolidation casting of oxide ceramics—Achievements and problems," *J. Eur. Ceram. Soc.*, **27** [2-3] 669–672 (2007).
- 17 S. Fakhfakh and S. Baklouti, "Elaboration and characterisation of low cost ceramic support membrane," *Adv. Appl. Ceram.*, **109** [1] 31–38 (2010).
- 18 L. Palacio, Y. Bouzerdi, M. Ouammou, A. Albizane, J. Bennazha, A. Hernandez, and J.I. Calvo, "Ceramic membranes from Moroccan natural clay and phosphate for industrial water treatment," *Desalination*, **245** [1-3] 501–507 (2009).
- 19 E. Chevalier, D. Chulia, C. Pouget, and M. Viana, "Fabrication of porous substrates: a review of processes using pore forming agents in the biomaterial field," *J. Pharm. Sci.*, **97** [3] 1135–1154 (2008).
- 20 S. Bose and C. Das, "Preparation and characterization of low cost tubular

- ceramic support membranes using sawdust as a pore-former," *Mater. Lett.*, **110** 152–155 (2013).
- 21 P. Belibi Belibi, M.M.G. Nguemtchouin, M. Rivallin, J. Ndi Nsami, J. Sieliechi, S. Cerneaux, M.B. Ngassoum, and M. Cretin, "Microfiltration ceramic membranes from local Cameroonian clay applicable to water treatment," *Ceram. Int.*, **41** [2] 2752–2759 (2015).
- 22 M. Felipe-Sesé, D. Eliche-Quesada, and F.A. Corpas-Iglesias, "The use of solid residues derived from different industrial activities to obtain calcium silicates for use as insulating construction materials," *Ceram. Int.*, **37** [8] 3019–3028 (2011).
- 23 C.N. Djangang, A. Elimbi, U.C. Melo, G.L. Lecomte, C. Nkoumbou, J. Soro, J.P. Bonnet, P. Blanchart, *et al.*, "Sintering of clay-chamotte ceramic composites for refractory bricks," *Ceram. Int.*, **34** [5] 1207–1213 (2008).
- 24 M. Dimitrijevic, R.J. Heinemann, D. Mitrakovic, and M. Gajic-Kvascev, "Influence of Preparation Conditions of Alumina-Based Refractory on the Morphological Parameters of Surface Defects," *Int. J. Appl. Ceram. Technol.*, **12** [3] 598–607 (2015).
- 25 M.-M. Lorente-Ayza, M.J. Orts, V. Pérez-Herranz, and S. Mestre, "Role of starch characteristics in the properties of low-cost ceramic membranes," *J. Eur. Ceram. Soc.*, **35** [8] 2333–2341 (2015).
- 26 H. Giesche, "Mercury Porosimetry: A General (Practical) Overview," *Part. Part. Syst. Charact.*, **23** [1] 9–19 (2006).
- 27 K.S. Sing, "Characterization of porous materials: past, present and future," *Colloids Surfaces A Physicochem. Eng. Asp.*, **241** [1-3] 3–7 (2004).
- 28 International Standard, "Ceramic tiles. Part 3: Determination of water absorption,

1
2
3
4 apparent porosity, apparent relative density and bulk density. (ISO 10545-
5 3:1995), including technical corrigendum 1:1997).,” *UNE-EN ISO 10545-31997*,
6 (1997).
7
8
9

10
11 ²⁹ P.A. Webb and C. Orr, *Analytical methods in fine particle technology*. Norcross,
12 USA, 1997.
13

14
15 ³⁰ A. Escardino, J.L. Amorós, M.J. Orts, and V. Beltrán, “Influence of pressing
16 variables on air permeability of fired floor tile bodies;” pp. 309–318 in *Sci.*
17 *Whitewares II*. Edited by W.M. Carty and C.W. Sinton. Wiley-American
18 Ceramic Society, Westerville, Ohio, 2000.
19

20
21 ³¹ J.L. Amorós, M.J. Orts, J. García-Ten, A. Gozalbo, and E. Sánchez, “Effect of
22 the green porous texture on porcelain tile properties,” *J. Eur. Ceram. Soc.*, **27** [5]
23 2295–2301 (2007).
24
25

26
27 ³² M.C. Martí-Calatayud, M. García-Gabaldón, V. Pérez-Herranz, S. Sales, and S.
28 Mestre, “Ceramic anion-exchange membranes based on microporous supports
29 infiltrated with hydrated zirconium dioxide,” *RSC Adv.*, **5** [57] 46348–46358
30 (2015).
31
32

33
34 ³³ S. Mestre, S. Sales, M.D. Palacios, M.-M. Lorente-Ayza, G. Mallol, and V.
35 Pérez-Herranz, “Low-cost inorganic cation exchange membrane for
36 electro dialysis: optimum processing temperature for the cation exchanger,”
37 *Desalin. Water Treat.*, **51** [16-18] 3317–3324 (2013).
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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.

Chamotte Reference	Starch type	Starch content (%)	Agglomeration method	Sintering temperature (°C)
0S-D	-	0	D	1050, 1100, 1150, 1200
10S1-D	S1	10	D	1050, 1100, 1150, 1200
10S2-D	S2	10	D	1050, 1100, 1150, 1200
10S3-D	S3	10	D	1050, 1100, 1150, 1200
10S2-W1	S2	10	W1	1050, 1100, 1150, 1200
10S1-W2	S1	10	W2	1050, 1100, 1150, 1200
10S2-W2	S2	10	W2	1050, 1100, 1150, 1200
10S3-W2	S3	10	W2	1050, 1100, 1150, 1200
30S1-D	S1	30	D	1200
30S1-W2	S1	30	W2	1200

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

Membrane	C0	A0	D0	E0	B0
Clay (%wt)	34	34	34	34	34
Na Feldspar (%wt)	34	34	34	34	34
Feldspatic sand (%wt)	17	17	17	17	17
Chamotte 10S1-W2 (%wt)	-	15	-	-	-
Chamotte 10S2-W2 (%wt)	-	-	-	15	-
Chamotte 10S3-W2 (%wt)	-	-	-	-	15
Chamotte 10S1-D (%wt)	15	-	-	-	-
Chamotte 10S2-D (%wt)	-	-	15	-	-

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

Series	R		A			B			C		
Membrane	R1	R2	A1	A2	A3	B1	B2	B3	C1	C2	C3
Clay (%wt)	40	40	28	22	16	28	22	16	28	22	16
Na Feldspar (%wt)	40	-	28	22	16	28	22	16	28	22	16
Feldspatic sand (%wt)	20	-	14	11	8	14	11	8	14	11	8
Chamotte 10S1-W2 (%wt)	-	60	30	45	60	-	-	-	-	-	-
Chamotte 10S3-W2 (%wt)	-	-	-	-	-	30	45	60	-	-	-
Chamotte 10S1-D (%wt)	-	-	-	-	-	-	-	-	30	45	60

Table IV. Starches characterization.

Reference	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D _V (μm)	D _S (μm)	Moisture (%)	Ash content (%)
S1	26	46	76	49	41	22.3	0.71
S2	16	75	184	90	35	8.7	3.53
S3	20	63	136	72	33	4.5	0.46

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

T (°C)	Weight loss (%)		
	10S1-D	10S2-D	10S3-D
1050	17.23	18.60	19.28
1100	18.39	18.94	19.34
1150	18.30	19.68	19.33
1200	18.18	18.94	19.37

Table VI. Characteristic pore diameters, total pore volume and BET surface area for chamottes obtained at 1200 °C from agglomerates prepared with 90 wt% clay + 10 wt% starch.

Chamotte	S_{BET} ($m^2 \cdot g^{-1}$)	d_{16} (μm)	d_{50} (μm)	d_{84} (μm)	Total pore volume V_T ($cm^3 \cdot g^{-1}$)
10S1-D	0.43	21.75	9.10	2.88	0.641
10S2-D	0.31	23.74	12.85	6.28	0.779
10S3-D	0.37	31.94	13.53	3.60	0.769
10S1-W2	0.59	31.83	7.66	2.25	0.714
10S2-W2	0.50	22.55	8.48	2.88	0.674
10S3-W2	0.16	30.01	18.32	8.38	0.554

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

Membrane	R1	R2	A1	A2	A3	B1	B2	B3	C1	C2	C3
Green density ($g \cdot cm^{-3}$)	1.87	1.59	1.67	1.55	1.48	1.81	1.75	1.70	1.70	1.62	1.55

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

Membrane	d_{16} (μm)	d_{50} (μm)	d_{84} (μm)	Total pore volume ($cm^3 \cdot g^{-1}$)	Water permeability ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$)	Open porosity (%)
A3	2.37	1.85	1.17	0.213	1390	35
B3	3.01	2.25	1.21	0.140	1190	26
C3	1.89	1.52	0.92	0.177	920	31

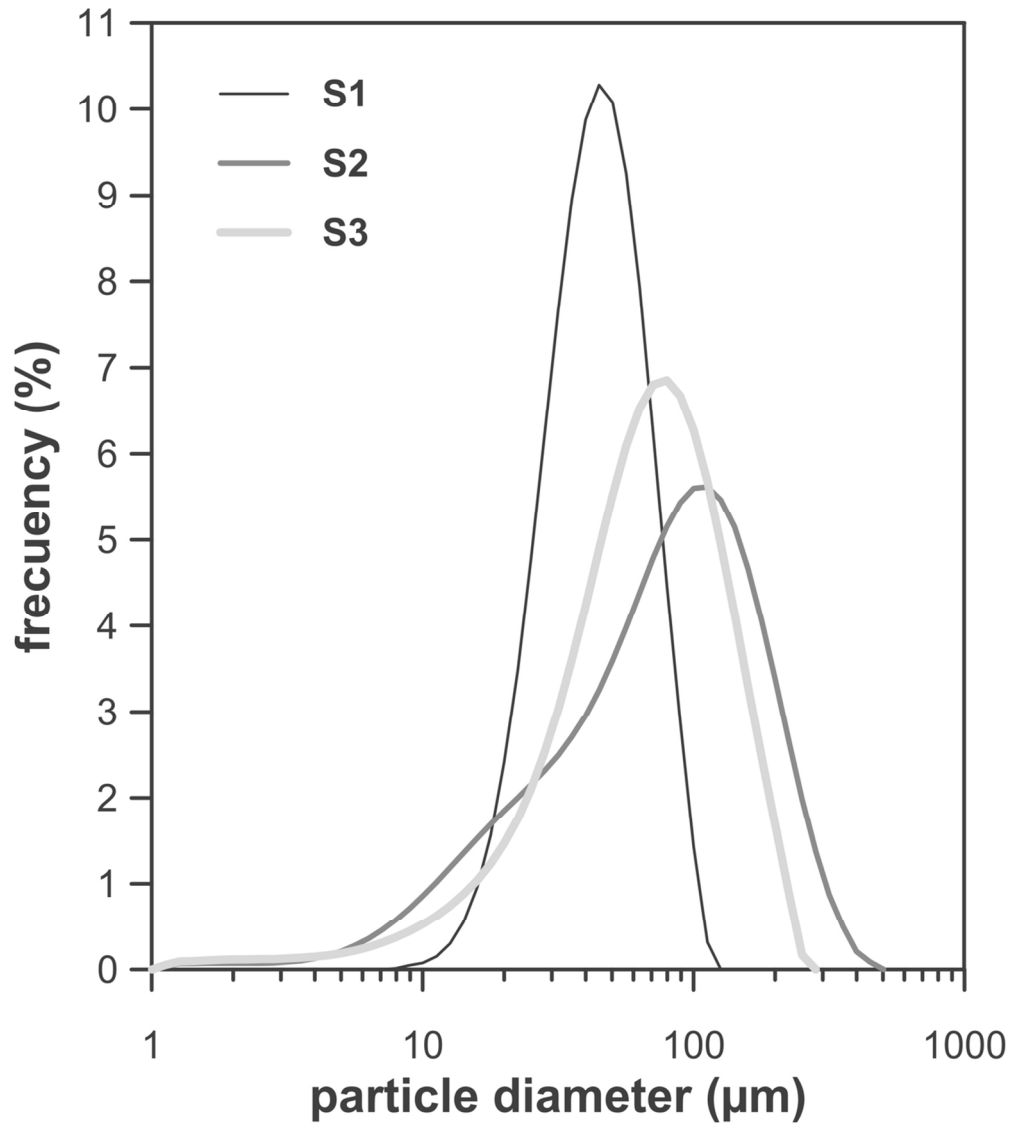


Figure 1. Starches' particle size distributions.

Figure 1

57x64mm (600 x 600 DPI)

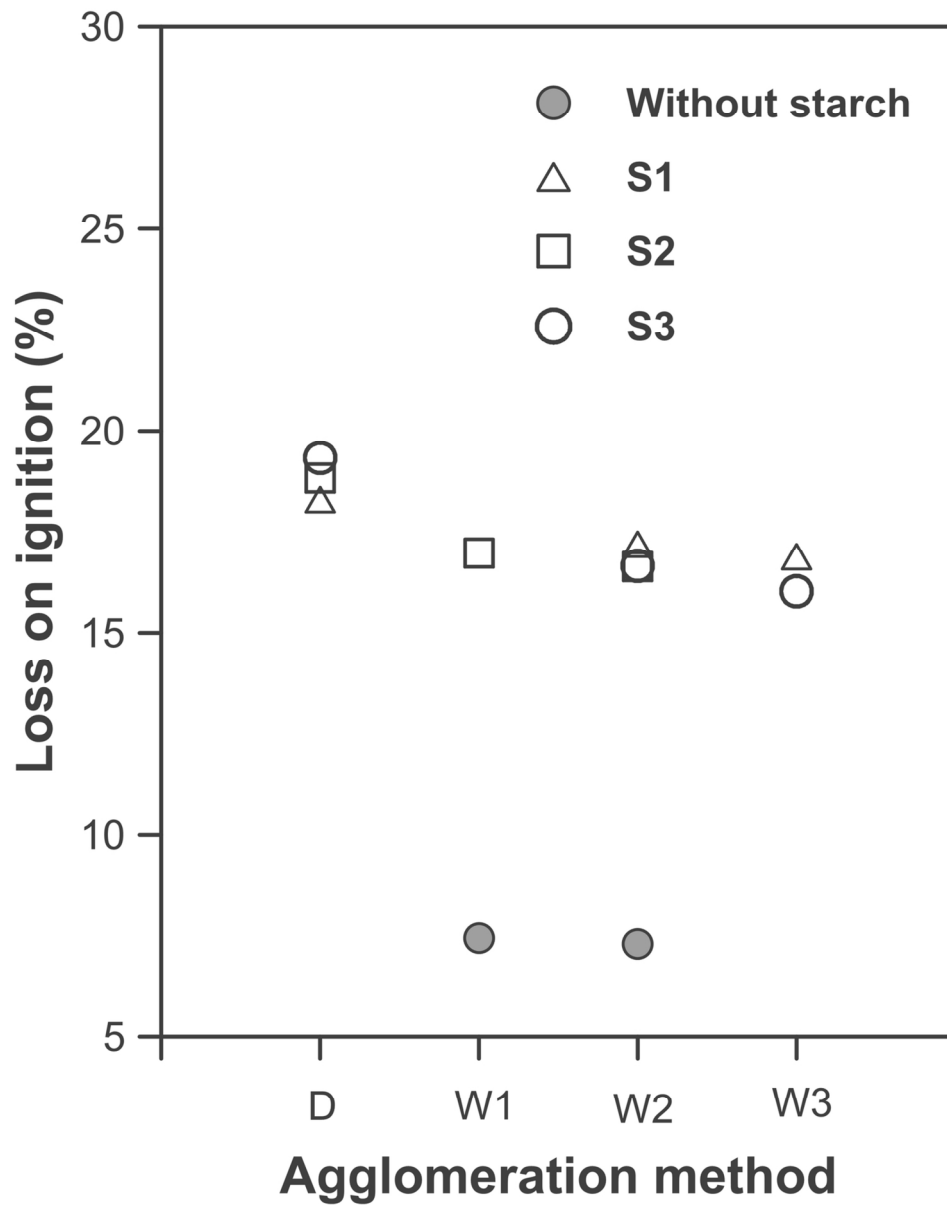


Figure 2. Mean weight loss of the agglomerates used to synthesize the chamottes.

Figure 2

64x80mm (600 x 600 DPI)

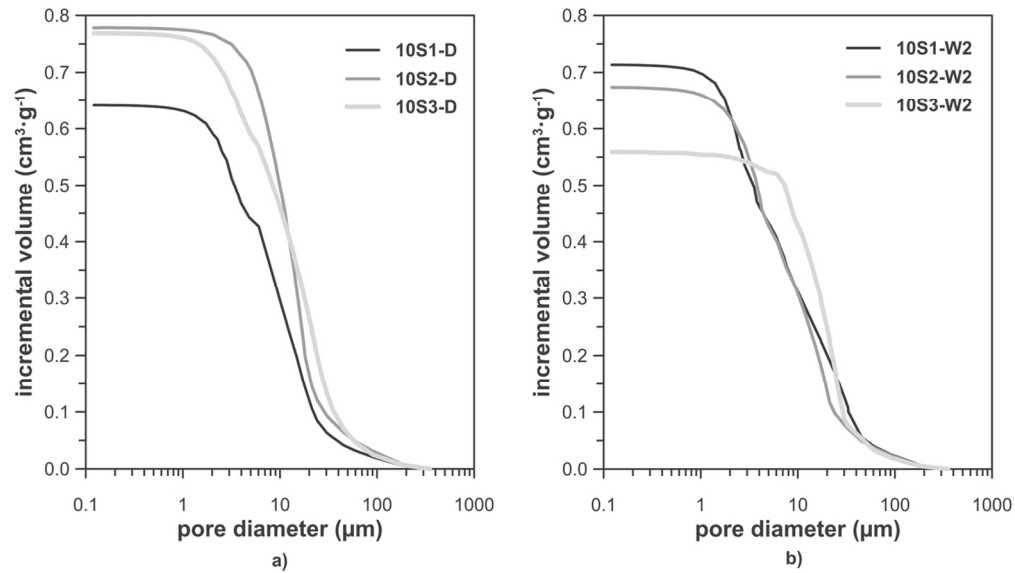


Figure 3. Pore size distribution of chamotte granules prepared with S1, S2 and S3 starches by dry (D) (a), and wet (W2) (b) method and fired at 1200 °C.

Figure 3

57x32mm (600 x 600 DPI)

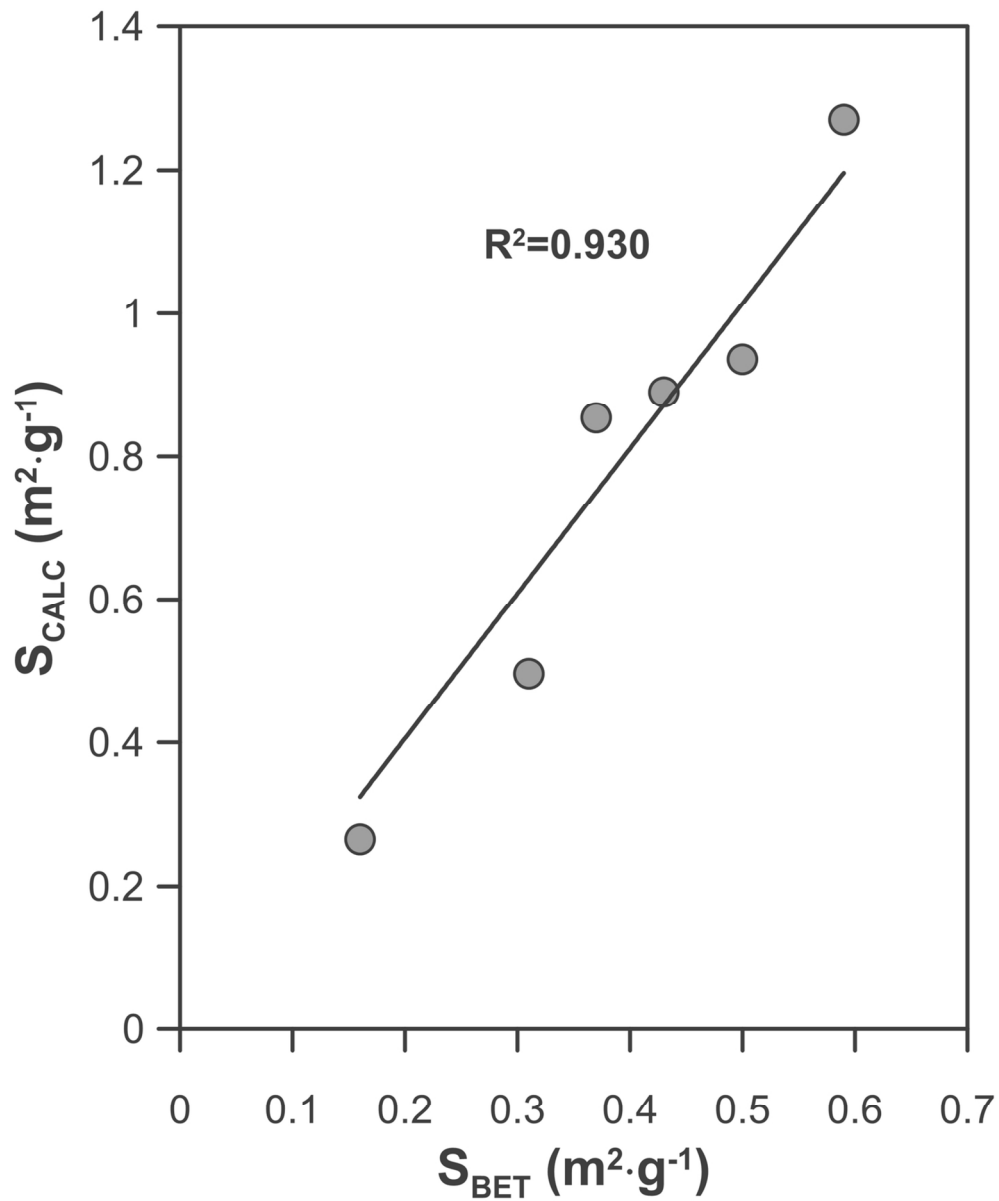
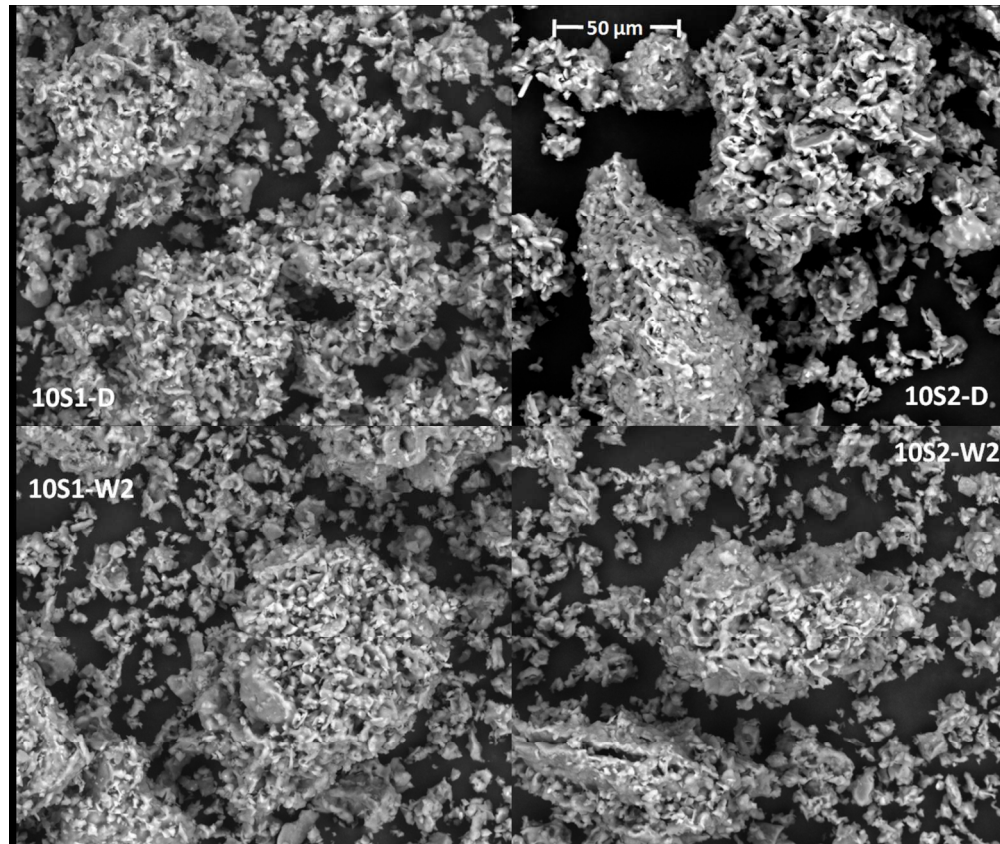


Figure 4. Equivalent surface area from mercury porosimetry versus BET area values.

Figure 4

61x74mm (600 x 600 DPI)



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

37 Figure 5
38 170x143mm (300 x 300 DPI)

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

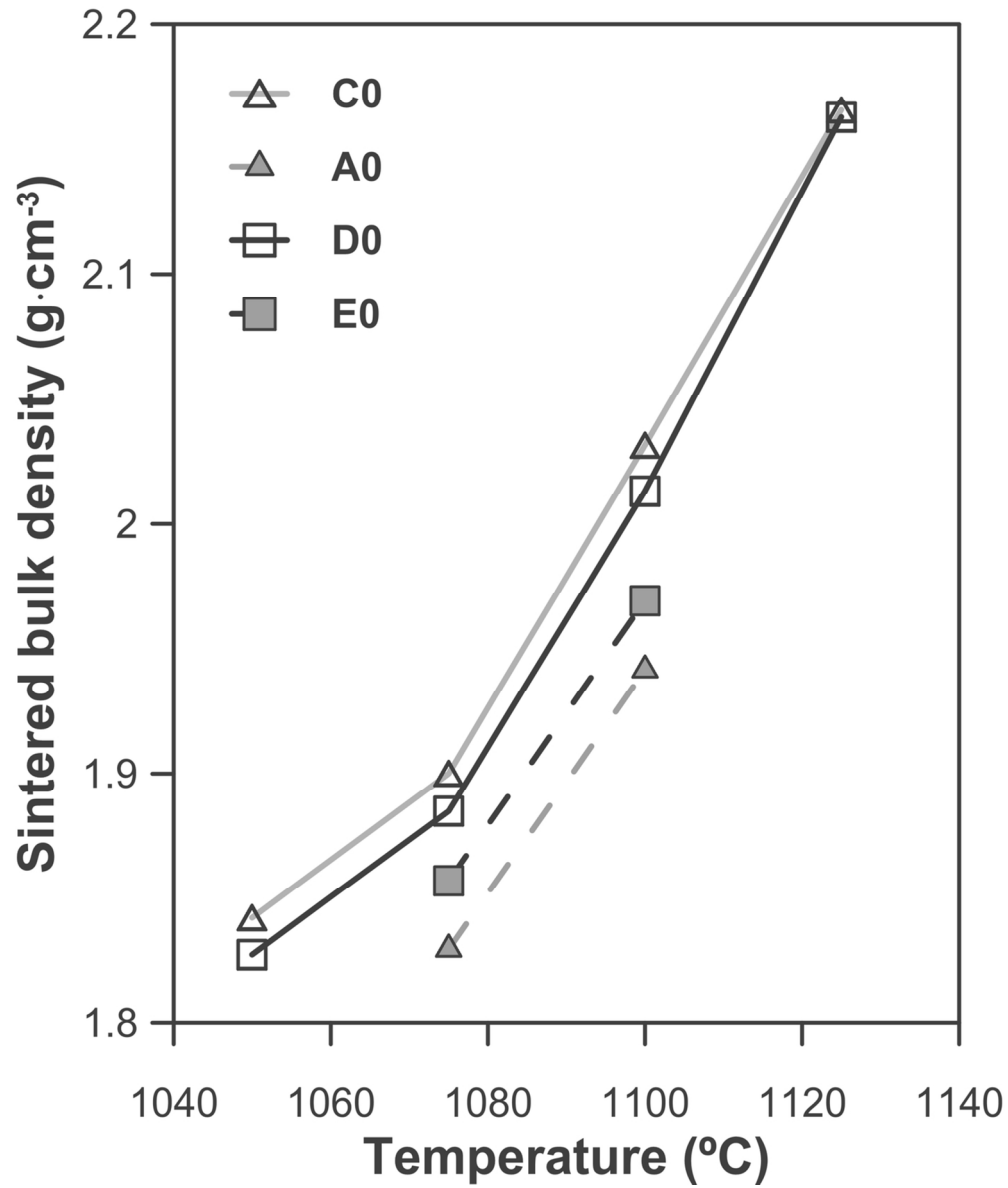


Figure 6. Bulk density of the membranes with 15 wt% chamotte.

Figure 6

60x71mm (600 x 600 DPI)

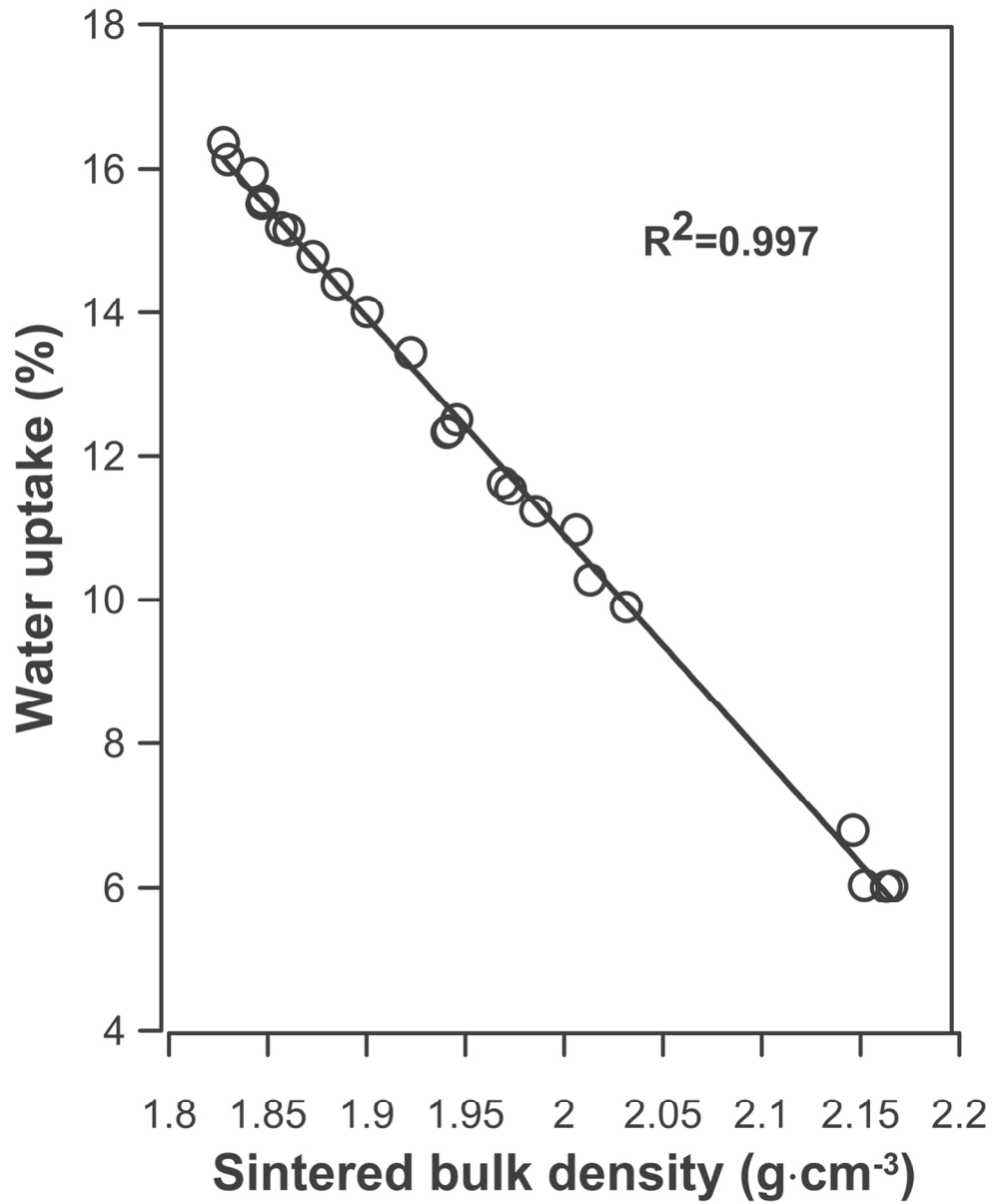


Figure 7. Open porosity, measured as water absorption, versus bulk density of membranes with 15 wt% of chamotte.

Figure 7

61x74mm (600 x 600 DPI)

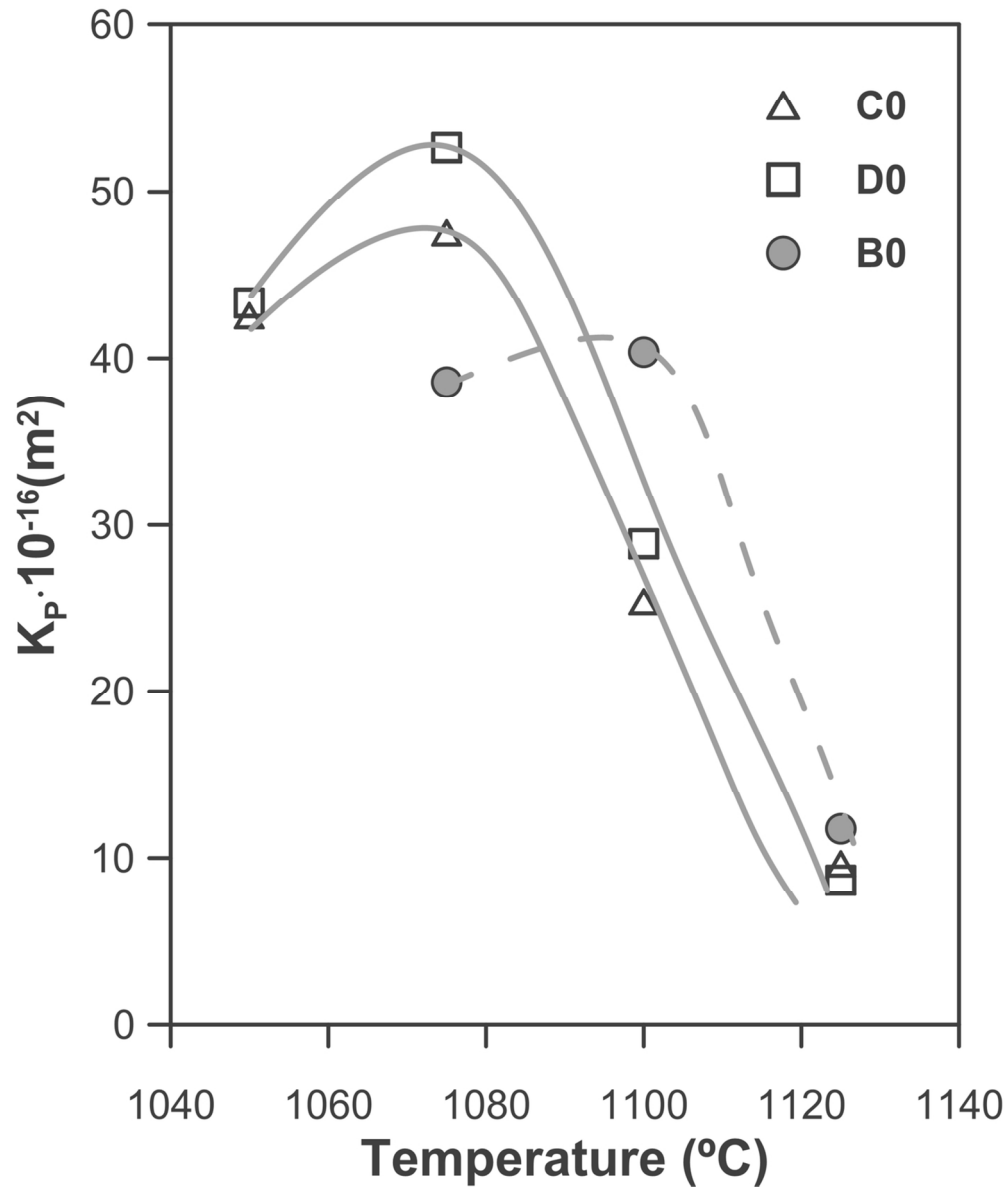


Figure 8. Variation of permeability with firing temperature for membranes prepared with 15 wt% of 10S1-D (C0), 10S2-D (D0) and 10S3-W2 (B0) chamottes.

Figure 8
60x71mm (600 x 600 DPI)

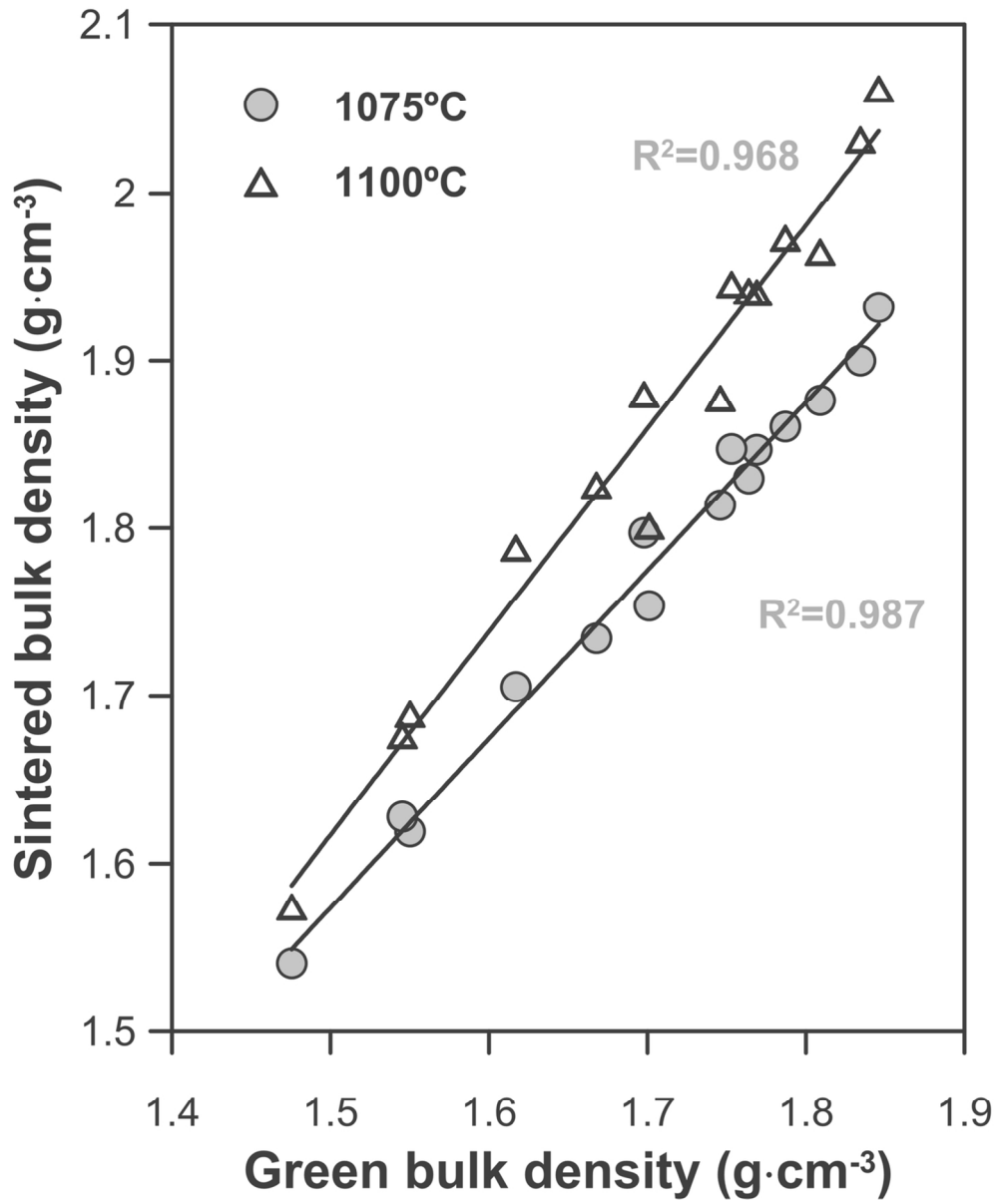


Figure 9. Bulk density of the membranes fired at 1075 and 1100 °C.

Figure 9

61x74mm (600 x 600 DPI)

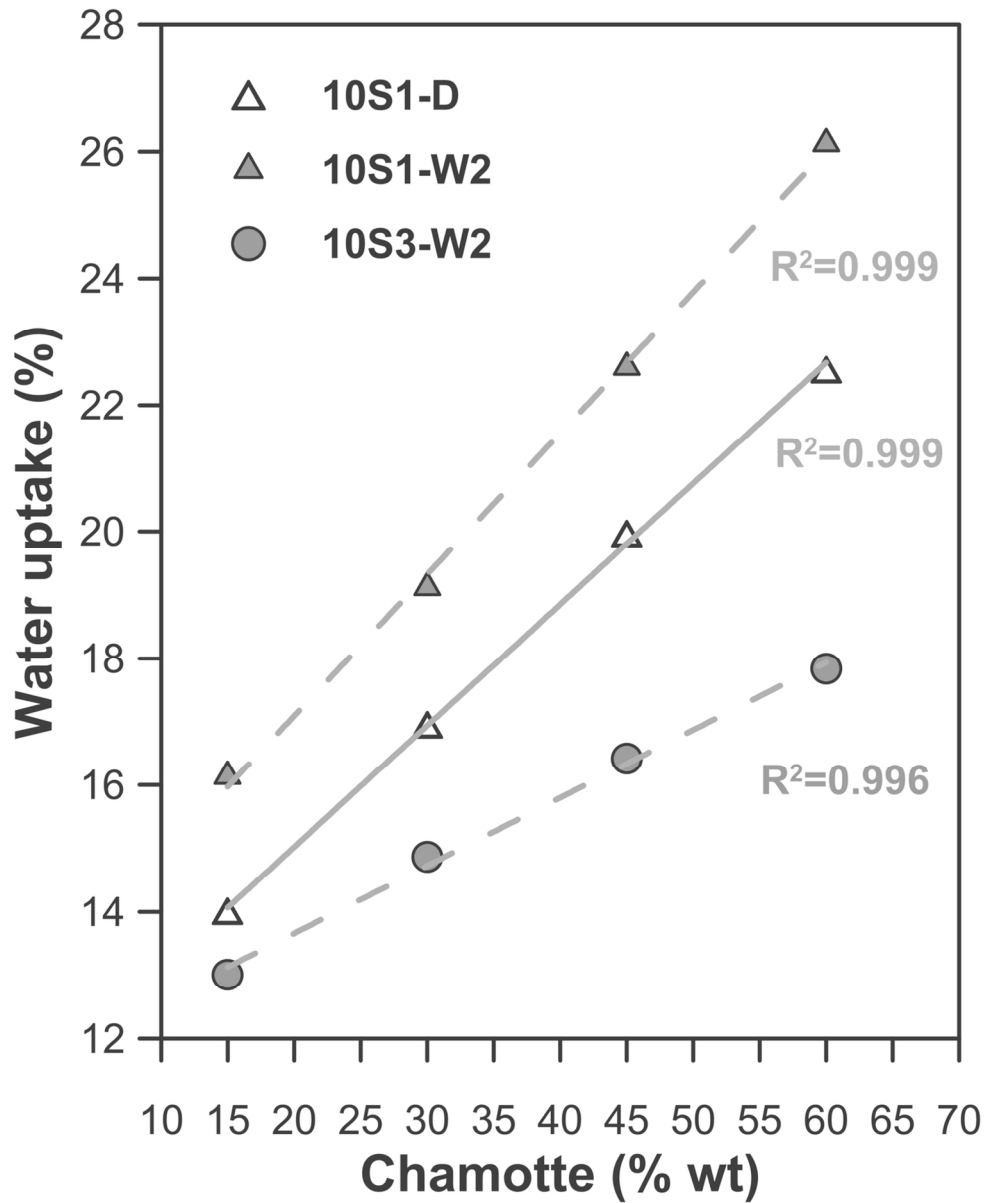


Figure 10. Variation of the open porosity of the membranes fired at 1075 °C with their chamotte content.

Figure 10

62x77mm (600 x 600 DPI)

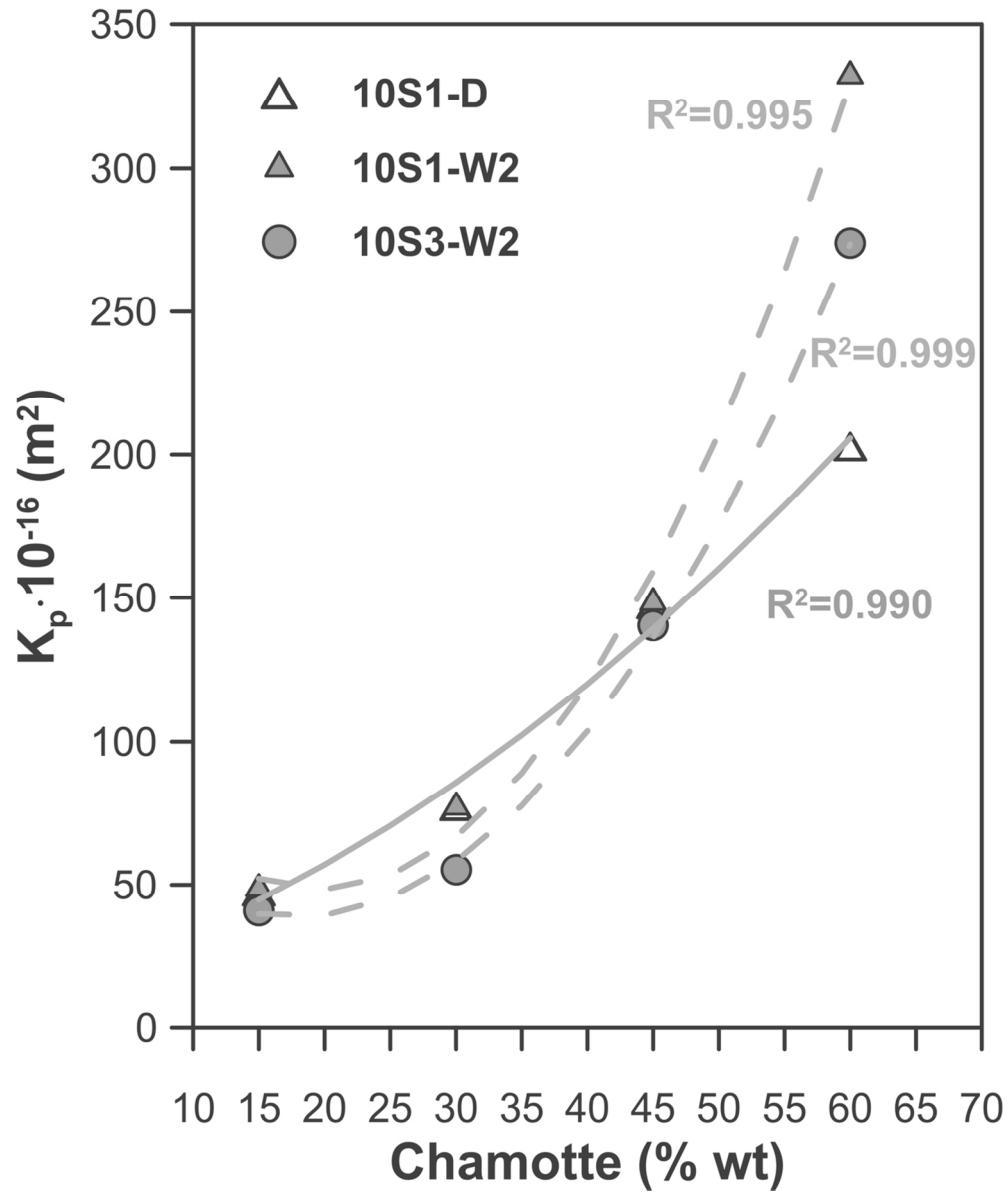


Figure 11. Variation of the water permeability of the membranes fired at 1075 °C with their chamotte content.

Figure 11

60x71mm (600 x 600 DPI)