

EFFECTS OF THE SINTERING TEMPERATURE ON THE PROPERTIES OF POROUS CERAMIC MEMBRANE SUPPORT MADE OF FLY ASH, KAOLIN, AND CLAYSTONE

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ABSTRACT

In this article, the influence of the sintering temperature on the properties of porous ceramic membrane support made of low-cost inorganic materials is reported. Fly ash was used as a dominant component since it presents cheap, abundant waste material and can be activated by alkalis to form porous structure with great mechanical resistance. Fly ash from coal combustion and additives, which consist of natural kaolin and claystone, were mixed with 5M NaOH solution to make a paste suitable for extrusion. Properties of created tubular porous supports, sintered at temperature ranging from 900 to 1100 °C, were characterized using a number of methods. Tubes sintered at 1000 °C were selected for microfiltration purpose. The morphology of the surface of these samples, studied by scanning emission microscopy (SEM) show homogeneous and crack free structure. Mercury porosimetry indicates uniform pore size distribution with average pore size value of 2.5 µm and pore volume of 38 % and show good mechanical resistance (7.7 MPa). These properties make fly ash-based ceramics suitable as membranes supports for microfiltration membranes technology.

Keywords: Ceramics; Fly ash; Membrane support; Sintering.

1 INTRODUCTION

Ceramic membranes systems, used for industrial wastewater treatment, recovery and reuse, represent one of the most important technologies that have gained popularity over past two decades. There is lot of data proving ceramic membranes dominance over polymeric ones especially when hot, corrosive, or oily wastewaters are treated [1–3].

Ceramic membranes for effluent filtration usually consist of three filtration layers, porous support, which provides mechanical strength to a membrane layer, interlayer, and a top separation layer. All layers are of different densities and decreasing thickness and can be made of the same or different material. Despite mentioned benefits, their wider application is limited mainly by the high prices of input materials and the cost of sintering processes.

Coal combustion product (fly ash) and natural materials (kaolin and claystone powders), all produced in the Czech Republic, were chosen as input materials in this study. The chemical composition of selected solid powder materials is mainly composed of silicon oxides (SiO₂) and aluminium (Al₂O₃) compounds. These aluminosilicates, in presence of alkali solution, are subject to geopolymerization process described by Davidovits [4]. The alkaline activation of aluminosilicates can be defined as a chemical process that leads to a rapid change in the specific structure – partially or totally amorphous which is very similar to the chemistry involved in the synthesis of large group of zeolites [4,5]. It was found that fly ash based geopolymer matrix after heat treatment to 1000 °C creates

a large number of small highly-dispersed pores and shows excellent results with high compressive strength, high temperature, and resistance to harsh environments [6–8]. Such characteristics are very useful for ceramic membranes supports. Geopolymer technology has also the potential to reduce the final cost of membranes supports preparation due to fact, that it does not require such high temperature calcining [7, 9]. In the ceramic membrane production, high sintering temperatures in range of 1100 to 1400 °C are usually needed to create satisfactory resistant and porous structure [10–14].

The main purpose of this study was to evaluate the influence of the relatively low sintering temperatures (900–1100 °C) on the resulting characteristics of ceramic membrane support prepared solely from cheap inorganic materials (fly ash, kaolin and claystone and NaOH solution) with no need of adding special organic additives or plasticizers. The optimal sintering temperature was determined with respect to the achieved results (phase formation, microstructure, porosity, and mechanical resistance).

2 EXPERIMENTAL

2.1 Support preparation process

For tubular support preparation, fly ash, kaolin, and claystone were used in volume ratio 5/4/1. The powders were mixed and a solution of 5M NaOH was added in an appropriate portion to make the dough suitable for extrusion. The paste was left for one hour to mature. After ageing phase, the tubes with a diameter of 25 mm were extruded with a laboratory extruder and left drying at laboratory temperature for 24 hours. The next day, sintering was performed. The main steps of the processing route for support preparation, used in this work, is described in Figure 1. Chemical analysis of the materials is given in our previous article [8].

Sintering experiments were carried out at temperatures 900 °C, 1000 °C, 1050 °C and 1100 °C for 2 hours and with temperature rise of 3 °C/min. The sintering temperature is a significant parameter that controls primarily the pore diameter, porous volume and also its mechanical resistance. The effect of different temperature on final support morphology, pore diameters, porosity, and mechanical strength was investigated.

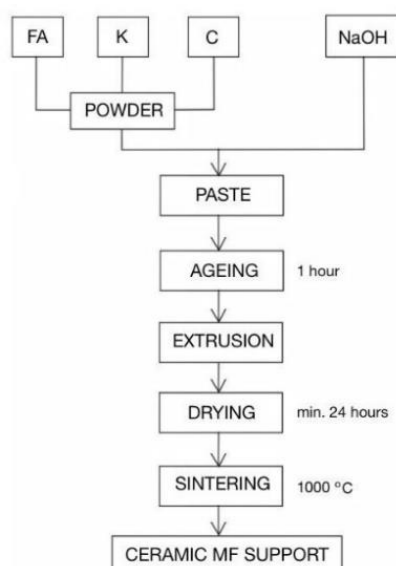


Figure 1. A schematic diagram of processing route for support preparation with chosen temperature of 1000 °C. (FA – fly ash, K – kaolin, C – claystone, MF – microfiltration)



Figure 2. Final support sintered at 1000 °C

3 RESULTS AND DISCUSSION

3.1 Characterization of the support

The most important properties for the prepared support are the pore size distribution, porosity, mechanical resistance, and overall support structure. All these characteristics have been tested to evaluate the suitability of the material as a membrane support for wastewater treatment.

3.1.1 Phase transformation

To understand the changes in the structure after alkali activation and sintering process, the phases identification using X-ray diffractometry (XRD) was performed. XRD data for unsintered and sintered samples at different temperatures are shown in Figure 3. Zincite is intended to quantify the amorphous content and is therefore included in the results of the quantitative analysis.

The presence of the amorphous phase is about 50 % in all samples. The crystalline phase consists mainly of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The presence of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is detected only in unsintered sample. The other crystalline phases identified were quartz (SiO_2), nepheline ($\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{13}$), cristobalite (tetragonal SiO_2), magnetite (Fe_3O_4), hematite (Fe_2O_3) and in the sintered samples labradorite $[(\text{Na},\text{Ca})(\text{Si},\text{Al})_4\text{O}_8]$.

Kaolinite, present in unsintered sample, is decarboxylated at higher temperatures and high-temperature reactions lead to the formation of mullite (Table 1). Mullite content increases slightly with the sintering temperature. It cannot be excluded that SiO_2 from crystalline phases (quartz and cristobalite), the amount of which decreases during sintering, also turns into mullite. As the temperature rises, the presence of the labradorite occurs and its content increases. Also, the amount of hematite increases with sintering temperature. However, its content is negligible and does not influence the final structure of the support.

The content of the amorphous component increased up to temperature of 1000 °C because the structure of amorphous metakaolin (product of kaolin calcination) is stable up to this temperature [15]. The disintegration of metakaolin activates mullite crystallization. After exceeding the temperature of 1000 °C, the content of the amorphous component decreases and the proportion of mullite increases (Table 1). The elevated temperature increased the propensity towards the formation of crystalline phases such as nepheline [6]. The presence of nepheline was confirmed in the sintered samples, but at higher sintering temperatures the contents of nepheline as well as cristobalite decreased, because it dissolves in the melt. Phases identified during sintering process promises good physical and mechanical properties of created supports.

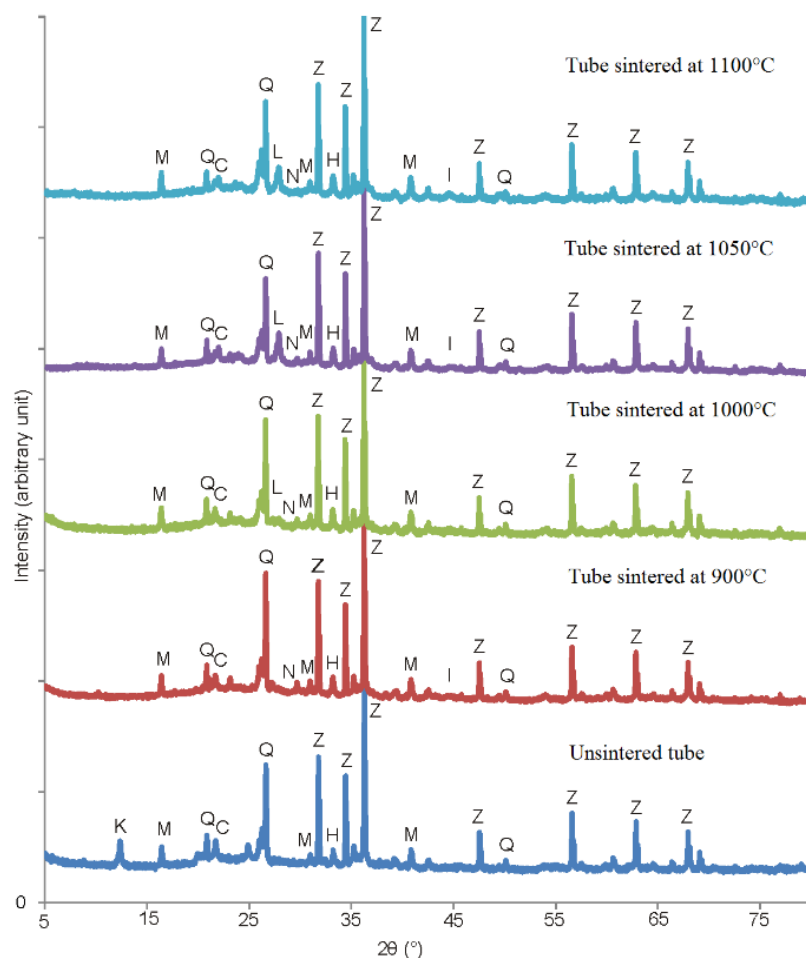


Figure 3. XRD data for unsintered and sintered samples at different temperatures. Mullite (M), kaolinite (K), labradorite (L), quartz (Q), nepheline (N), cristobalite (C), hematite (H), magnetite (M) and zincite (Z)

Table 1. Content of the crystalline phases and amorphous component in unsintered and sintered samples at different temperatures

Contents of the crystalline phases and amorphous component (wt %)									
Support	Mullite	Kaolinite	Labradorite	Quartz	Nepheline	Cristobalite	Hematite	Magnetite	Amorph
Unsintered	20.33	10.45	-	8.29	-	5.29	0.82	0.26	54.56
Sintered at 900 °C	21.63	-	-	8.38	5.37	2.50	1.39	0.58	60.15
Sintered at 1000 °C	22.32	-	2.40	7.96	3.28	2.17	1.46	-	60.41
Sintered at 1050 °C	22.89	-	13.04	7.11	2.27	1.86	1.73	-	51.10
Sintered at 1100 °C	26.98	-	11.60	6.18	-	1.67	2.44	0.17	50.96

3.1.2 Scanning electron microscopy (SEM)

The visual assessment of prepared tubes was done using scanning electron microscopy – SEM (FEI Quanta 650 FEG, USA). Figure 4 points at difference in microstructure in the dependence on the sintering temperature, an important parameter that controls the pore diameter of the support. Image (a) represents unsintered sample in which we can see ball-shaped grains typical for fly ash. This spherical structure is also seen in the image (b) that represents sample sintered at 900 °C. As the temperature rises, the individual grains melt down and structure becomes smooth, homogeneous, and porous. At sintering temperatures 1050 °C and 1100 °C melted structure can be seen and from the images (d) and (e) it is obvious that the number of the pores in material is decreasing while the size of the pore is increasing.

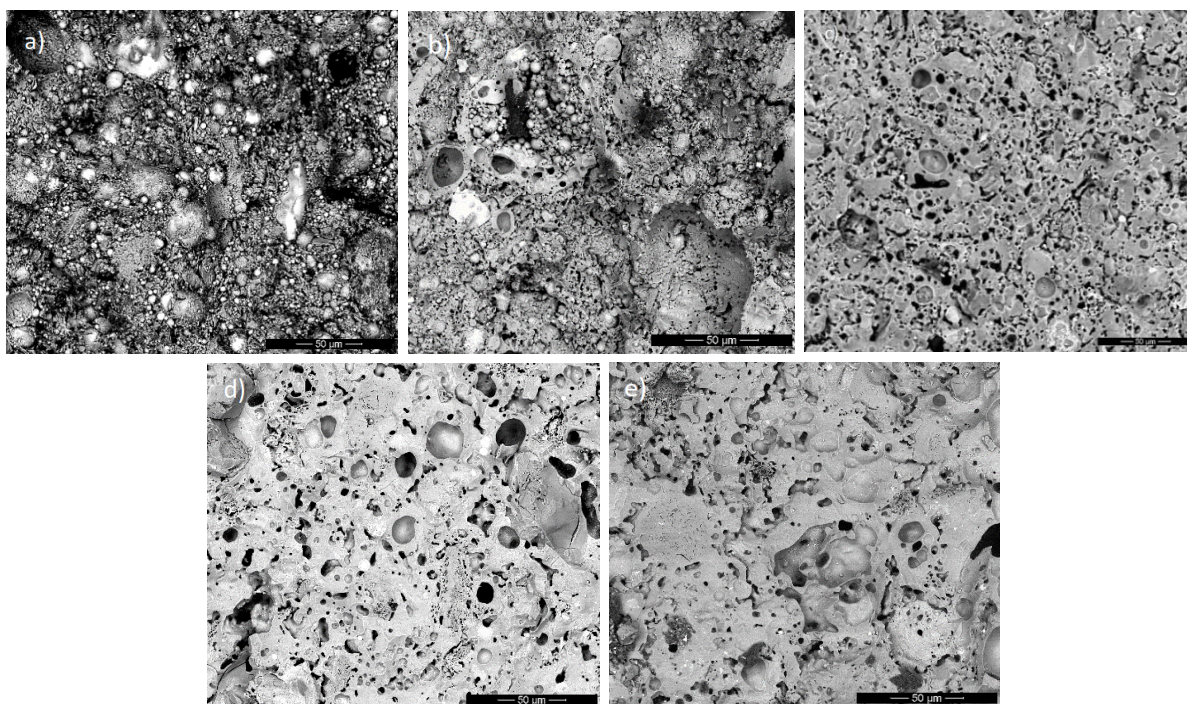


Figure 4. Microstructure of a) unsintered support, b) supports sintered at 900 °C, c) at 1000 °C, d) at 1050 °C, e) at 1100 °C

In the range of sintering temperature 1000 °C, the pore size and the porosity achieved the range that needed to be obtained. The morphology of sintered samples shows no defects such as cracks, and the surface is homogeneous and smooth. The inner structure is sufficiently uniform to apply the membrane separation layer.

3.1.3 Mercury porosimetry

The pore size distribution and the porosity of supports sintered at different temperatures was characterised by mercury porosimetry (AutoPore IV 9500, Micromeritics, USA). Figure 5 shows the relation between increasing sintering temperature and the average pore size diameter and pore volumes. The dependence confirms what was already reported by authors working with fly ash-based membranes, i.e., with increasing sintering temperature the average pore size increases and total porosity decreases [10,11].

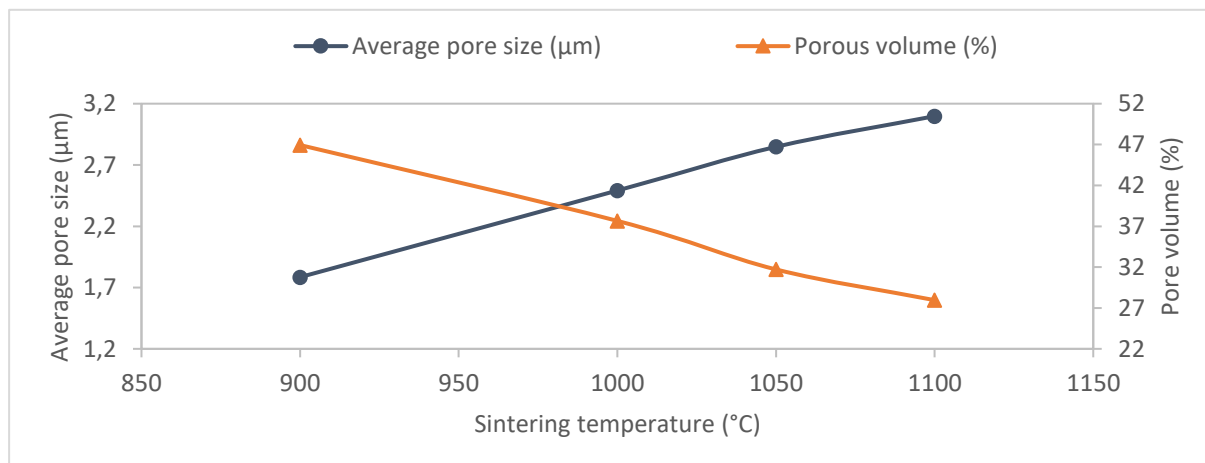


Figure 5. Average pore size and pore volumes vs. sintering temperature

Mercury porosimetry reveals the average pore size increase from approximately 1.7 to 3.1 μm and decrease in porosity from 47 % to 28 % with temperature rising from 900 °C to 1100 °C. At high temperatures, particles begin to melt reducing the pore volume and lead to the formation of large pores and elimination of small ones. The sintering temperature was optimised at 1000 °C for the produced supports. The supports sintered at this temperature presented optimal ratio of pore diameters and pore volume.

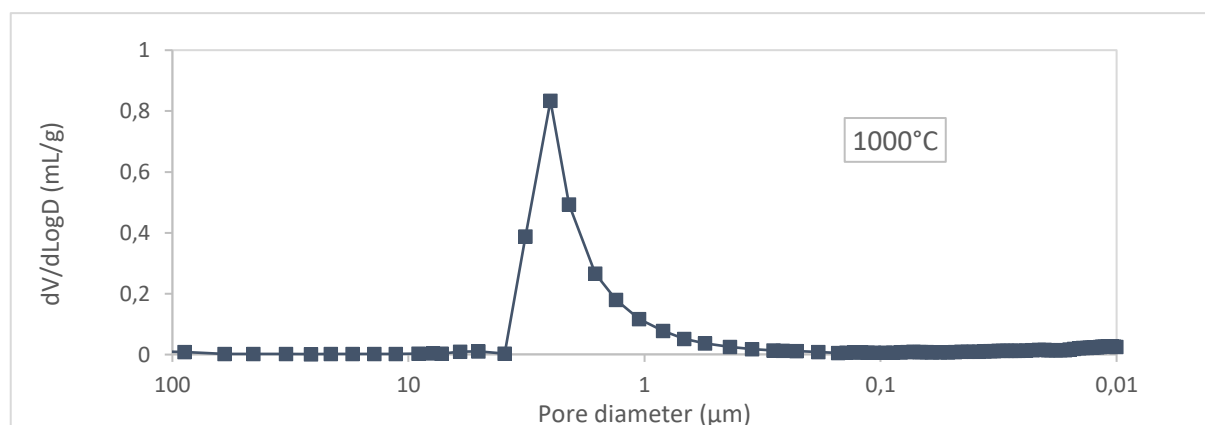


Figure 6. Pore diameters of support sintered at 1000 °C

Figure 6 presents pore size distribution for support sintered at 1000 °C and shows almost mono modal distribution of pore sizes. Average pore diameter was centred at 2.5 μm and the porous volume at this temperature was of 38 %. Monomodal pore size distribution reveals the success of sintering process and absence of cracks through the support.

3.1.4 Mechanical resistance

The measurement of the mechanical resistance of the sintered material was carried out by three-point bending method using MTS 816 Rock Test System, USA. The measurements were performed on sintered 40×10×5 mm test bars. The distance separating the two points was 30 mm and constant rate was set at 0.01 mm/s. Figure 7 shows the dependence of tensile strength with sintering temperature and indicates almost linear dependence. This

dependence is in correspondence with pores forming characterisation depicted in Figure 5. The increase of the temperature led to densification and consequently to an increase in tensile strength. More significant course of function was from 900 °C to 1000 °C (5.8 to 7.7 MPa) than from 1000 °C to 1100 °C (7.7 to 8.9 MPa). Dependences point out to general correlation between microstructural changes as pore size and total porosity and mechanical resistance [11–13]. However, most studies dealing with the preparation of supports from alternative materials work with temperatures up to 1400 °C. At 1100 °C the achieved mechanical strength values were comparable, namely 9.8 MPa found by Jedidi [11] or 8.5 MPa found by Bouzerara [13].

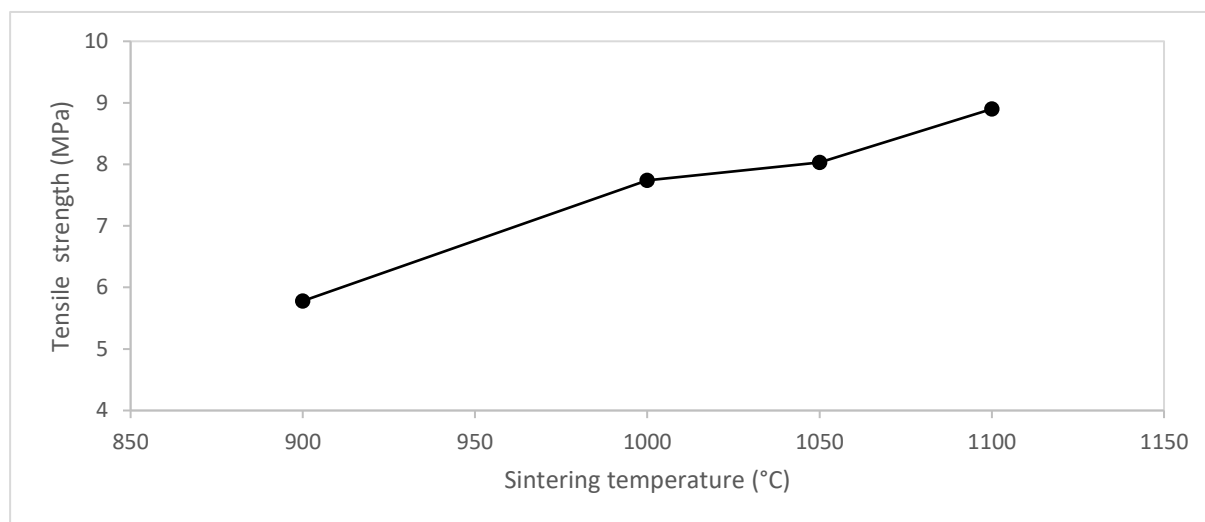


Figure 7. Tensile strength as a function of sintering temperature

4 CONCLUSIONS

The main goal of this study was to evaluate and optimize the sintering temperature in the preparation of porous ceramic membrane supports made of cheap inorganic materials. For the intended purpose, waste and natural products, fly ash, kaolin, and claystone, were used. These powder materials were mixed in appropriate ratio with alkaline solution to form paste suitable for extrusion, which met the conditions for microfiltration (MF) support such as porosity, pore volumes, crack-free surface, and mechanical stability. Alkaline activation led through geopolymerisation to formation of solid material that had to be strengthened by sintering. Effect of relatively low sintering temperatures of 900 °C, 1000 °C, 1050 °C and 1100 °C on overall support characteristics was studied. The optimal sintering temperature was determined comparing the tube structure, porosity, and tensile strength and was set to 1000 °C. At this temperature, the average pore size distribution of 2.5 µm and total porosity ratio of 38 % was reached. The mechanical resistance was 7.7 MPa. Scanning electron microscopy (SEM) showed uniform pore distribution and defect free structure. Based on these characteristics, it can be concluded that prepared fly ash based ceramic supports could be used for MF membrane production.

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