Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.871341

53 (2015) 1037–1044
January

Taylor & Francis
Taylor & Francis Group

Elaboration of membrane ceramic supports using aluminum powder

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Received 21 May 2013; Accepted 21 November 2013

ABSTRACT

In this paper, two different processing ways have been presented and have led to two support shapes with particular interest: tubular and flat configurations, which are currently the most used supports in membrane research. Porous cermet supports for membrane substrate in tubular and flat configurations have been prepared from kaolin and aluminum powder mixtures. Tubular configurations were produced by an extrusion method, whereas flat configurations were obtained by dry pressing. Our findings demonstrate that the addition of metal ratio to kaolin matrix has a positive effect on the porosity of supports compared to those prepared from kaolin alone and has two conflicting effects on mechanical strength. Moreover, in the presence of aluminum, the mechanical strength either increases or decreases according to the shape of the cermet support. On the other hand, open porosity and water permeability of the ceramic supports increase proportionally with the addition of aluminum ratio to kaolin matrix for tubular and flat configurations.

Keywords: Kaolin; Porous supports; Metal powder; Extrusion; Strength

1. Introduction

The development of new inorganic membranes is an interesting research field for the separation of small molecules in biotechnologies, pharmaceutics, chemical industries, water treatment, and also in gas separation and catalysis. The use of the membrane technology to replace a separation or purification step in existing industrial processes may reduce the overall consumption of energy and yield acceptable results.

Composite materials formed by an insulating ceramic matrix and metallic particles, also known as cermets, have recently attracted much attention due to singular combination of their mechanical and microstructural properties. Clay minerals are well-known for their structural adsorption, good rheological, and thermal properties [1,2]. As a consequence, clays as membrane materials have become the focal point of much research [3]. In previous studies, supports are generally manufactured from compounds such as alumina (Al_2O_3), cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), mullite ($3Al_2O_3{\cdot}2SiO_2$) [4–6], and Silicon carbide (SiC). Porous alumina ceramics, with both tubular and flat shapes,

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Presented at the International Joint CB-WR-MED Conference / 2nd AOP'Tunisia Conference for Sustainable Water Management, 24–27 April 2013, Tunis, Tunisia

are considered as supports for microfiltration or ultrafiltration membranes [7,8]. Some efforts have been made to prepare porous ceramic support by compacting and extrusion, using kaolin as the main raw material [6,9]. However, these prepared supports showed some shortcomings such as low porosity, small pore size, rigidity, and large shrinkage [9,10]. Porous ceramics can be made by adding pore-forming agents such as sawdust, starch, carbon, or organic particulates [11] into the starting powders, or by injection molding [12].

Through this study and in accordance with these ideas, we will try to present the role played by the additive aluminum powder in the formation of porosities in ceramic tube and flat supports elaborated by extrusion and molding methods, respectively, and also to monitor the evolution of the flexural mechanical strength and the open porosities in porous supports upon increasing the amount of metal powder.

2. Methods

2.1. Materials and chemicals

The preparation of tubular and cylindrical porous ceramic supports for membranes requires the skills in selecting the proper raw materials and the recipe. In this study, the used raw materials are: (1) kaolin powder supplied by BWW Minerals, with the chemical compositions listed in Table 1, (2) aluminum powder obtained from Merck with a purity of more than 99% and grain size of 100–200 μm, and (3) distilled water. All the materials were used as received.

2.2. Supports elaboration

The tubular porous supports were elaborated wet, whereas the flat ones were produced dry. Then, we describe the production method of each type:

2.2.1. Tubular porous supports

The objective of this part was to achieve tubular porous supports based on a mixture of kaolin and aluminum powders by the extrusion process. The elaboration of a ceramic porous supports was achieved as follows:

- Preparation of a plastic ceramic paste.
- Shaping by extrusion.
- Consolidation by thermal treatment.

The samples were synthesized from a mixture of kaolin and aluminum powders, this involves the preparation of a stable paste. Preliminary experiments indicated that a suspension of kaolin, aluminum, and water do not yield a plastic paste. This is due to the oxidation of aluminum in water to form aluminum hydroxide and hydrogen in the vicinity of room temperature according to the following chemical reaction [13]:

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2 \quad (1)$$

Experimental results from former investigations show that some surfactant phyllosilicates of the kaolinite group as well as some oxides like Al_2O_3 create foams by the formation of H_2 gas from the dissolution of aluminum in alkali free water-based suspensions at pH 7–9. Others have shown that porous light weight refractory materials can be produced according to the aerated concrete technology with metal powders or pastes based on aluminum serving as a pore-forming agent [14,15].

It is possible to minimize the pore-forming reaction by the dissolution of aluminum in acidified water. For this reason, we decided to prepare low pH paste-based suspension. To do this, a quantity of 350 g of kaolin and aluminum powders were uniformly mixed, then 500 ml of distilled water was added before mixing again. Previous preliminary studies have proven that the addition of an amount of acid was necessary to make a suspension with good plasticity. It was acidified with 1 M sulfuric acid at a pH value equal to 4. Before the extrusion phase, an aging stage of the aqueous suspension is necessary to obtain a good homogeneity and to favor the formation of porosities. This step is required to prepare a paste with rheological properties allowing the shaping by extrusion. To this end, the excess of liquid was eliminated and the obtained paste was kept in a closed plastic bag for 24 h under high humidity environment to avoid premature drying and

Table 1
Chemical composition of the used kaolin (wt.%)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	SO_3	L,O,I
wt.%	52.41	29.83	3.48	0.81	0.73	0.36	0.07	12.31

ensure a homogeneous distribution of additives. After aging, the paste was extruded into the tubular specimens through an extruder, then the wet pieces are set on stems at room temperature during 24 h to ensure a homogenous drying and to avoid twisting and bending. Finally, the specimens were thermally treated in a manufacturing furnace (Nabertherm) at 1,250˚C for 1 h with a ramping rate of 2˚C min^{-1} in order to avoid the formation of cracks on the layer, and then cooled to room temperature naturally. The support from kaolin was also prepared using the same processing conditions described above.

2.2.2. Flat porous supports

The following procedure for this type of samples was very quick and easy. Several flat disks (6 mm in thickness and 30mm in diameter) were prepared dry departing from kaolin powder homogeneously mixed with different ratios of aluminum powder without any water addition. The mixed powder was axially pressed at different strengths to get flat disks with different performances before they were sintered using a programmable furnace at 1,250˚C with a heating rate of 2˚C min^{-1} for 1 h.

2.3. Characterization techniques

In this study, X-ray diffraction (XRD), thermal analysis (DTA/TG), Mechanical strength, and permeability measurements have been used for a thorough characterization of the system.

Phase identification was performed by XRD analysis (Philips X'Pert X-ray diffractometer) with Cu kα radiation (λ = 1.5406 A˚), and the crystalline phases were identified by reference to the International Center for Diffraction Data cards.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out from ambient temperature to 1,300˚C at a rate of 10˚C min^{-1} under air, using a setaram SETSYS Evolution 1750.

Mechanical properties of the two sintered configurations were realized using a LLOYD EZ50 Instrument: The tubular ones were evaluated by the three points bending method applied to sintered test supports with a span length of 50 mm and crosshead speed of 1 mm/min. The bending strength, σ_f, was calculated using the following equation [16,17].

$$\sigma_f = \frac{8FLD}{\pi(D^4 - d_i^4)} \quad (2)$$

where F is the measured force at which a fracture takes place; L, D, and d_i are the length (in this case, 50 mm), the outside diameter, and the inner side diameter of the tube, respectively. Moreover, mechanical properties of the flat configurations were measured by the Brazilian test applied to sintered flat disks with a displacement rate of 0.5 mm/min. The maximum rupture strength, $\sigma_{r,}$ was determined following the elasticity theory [18]:

$$\sigma_r = \frac{2P_{\max}}{\pi LD} \quad (3)$$

where L and D are the sample length and the diameter, respectively, and $P_{\max}$ is the maximum applied load at failure. Generally, three samples of each composition elaborated under the same conditions were tested and an average value was then calculated.

The tangential filtration experiments were performed using a home-made pilot plant at room temperature. It is equipped with a cross-flow filtration system implementing the tubular ceramic tubes of 15 cm length of this work. The transmembrane pressure (TMP) can reach 9 bars which corresponds to the ultrafiltration range. It was controlled by an adjustable valve on the retentate side. The hydraulic permeability of the disk-shaped support was characterized using a dead-end filtration apparatus under TMP exceeding 3 bars which corresponds to the ultrafiltration range. A disk-shaped support was sealed in a stainless steel module using O-rings, so as to ensure a perpendicular direction of the liquid to the filter surface. Before the tests, the tubular and planar configurations supports have been conditioned by immersion in distilled water for at least 24 h to reach a stable flux at the beginning of the experiment [19]. The determination of permeability was performed with distilled water.

The open porosity of the two sintered configurations was measured by a water absorption test. The specimens were weighed in dry before the filtration test, then wiped clean of all surface water and weighed again. The open pore volume V_{op} (cm^3) corresponds to the volume of water absorbed by the sample. Since the density of water is 1 g/cm^3 at 4˚C, the difference in weight (g) of the sample before and after saturation corresponds to the open pore volume:

$$V_{\text{op}} = m_s - m_d \quad (4)$$

where m_s and m_d are the mass of the saturated and the dry sample, respectively. The percentage of the open porosity was calculated using the following formula:

$$\% \text{ Open porosity} = 100(V_{op}/V_a) \quad (5)$$

where V_{op} and V_a are the open pore and the apparent volume of the sample, respectively. One advantage of this method is that it measures only the accessible pores that are of relevance to membrane transport and another advantage is that it is not a destructive technique.

3. Results

3.1. Characterization of the starting materials

Fig. 1 presents the XRD patterns of the raw and thermally treated clay. Before applying heat treatment, it can be seen that kaolinite (K) was the major mineral component with a small amount of quartz (Q) and illite (I) impurities. No other components were observed, because the impurities are so tiny (see Table 1) and most of them are probably incorporated into the crystal structure of kaolinite [20]. After calcination of the sample at 600˚C, all the peaks in the diffractogram due to kaolinite disappeared. This is due to the transformation of kaolinite to amorphous metakaolinite [21]. On the contrary, the peaks of quartz and illite did not change, which means the kaolinite phase is only concerned by the thermal treatment at 600˚C. At a temperature of 1,250˚C, peaks of illite (I) disappeared too, whereas peaks of mullite (M) appeared due to the transformation of metakaolinite. The quartz peaks remained unchangeable in the diffractogram which confirms the thermal stability of this phase. During the thermal treatment of the sample (Fig. DTA/TG), different changes were observed which corroborates the evolution of XRD patterns.

XRD patterns of the pure aluminum powder is presented in Fig. 2, it includes two very high intensities and narrow peaks corresponding to aluminum phase. After mixing with kaolin and sintering at 1,250˚C for 1 h, Fig. 3, mullite is found to be the major phase constituent of the sample. The peaks' intensities of quartz and aluminum are weakened but still remain, which confirms the thermal stability of these phases.

The structural evolution of the powders evaluated by differential thermal and thermogravimetric analysis (DTA–TG) shows the temperature regimes, where predominant weight losses (and hence transformations) of kaolin, aluminum, and kaolin/aluminum mixture are observed. DTA and TG curves recorded during compact heating of the kaolin, aluminum, and kaolin/aluminum mixture are presented in Figs. 4–6, respectively. A total weight loss is observed to be about 12.5% of kaolin (Fig. 4). In fact, the weight loss consists of two distinct stages: The first one is considered as a slight weight loss between room temperature and 150˚C, because of the dehydration of the clay. The second mass loss detected between about 400 and 700˚C is mainly due to the phenomenon of dehydroxylation of kaolinite confirmed by DTA which shows an endothermic peak at 560˚C leading to the transformation of kaolinite to metakaolinite according to the following reaction [22].

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \text{ (kaolinite)} \longrightarrow Al_2O_3 \cdot 2SiO_2 \text{ (metakaolinite)} + 2H_2O \quad (6)$$

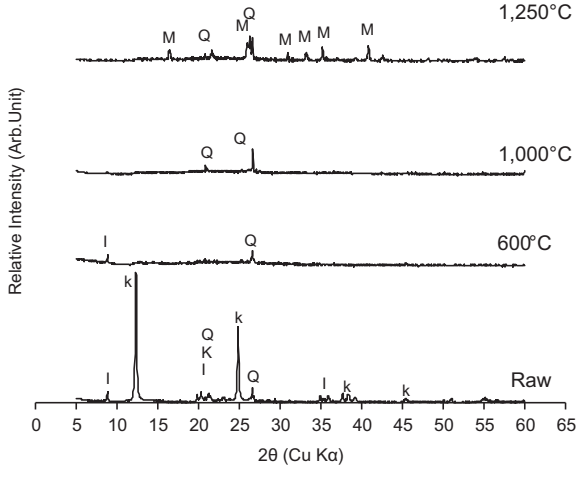

Fig. 1. XRD pattern of the pure kaolin before and after heat treatment (K = kaolinite, Q = Quartz, I = illite and M = Mullite).

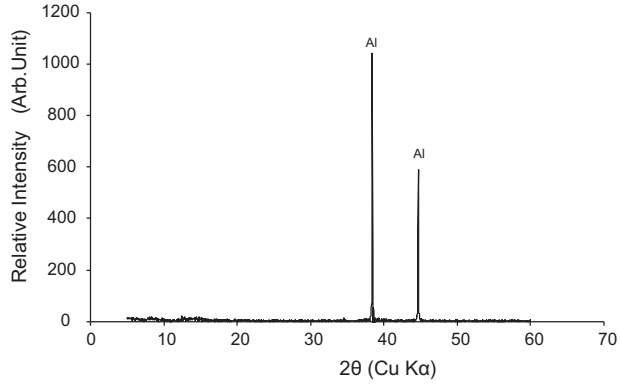

Fig. 2. XRD pattern of the pure aluminum (Al = aluminum).

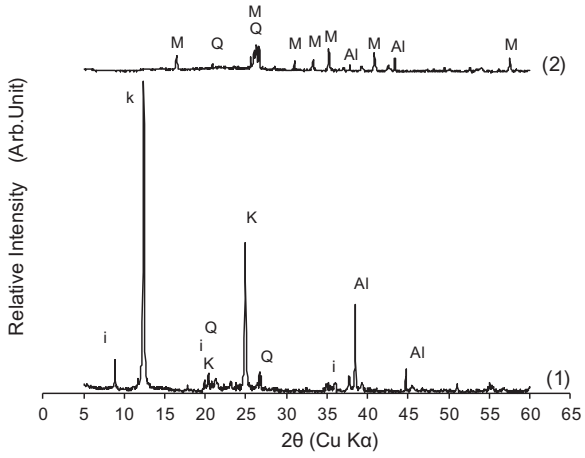

Fig. 3. XRD pattern of the mixture of kaolin/10 wt.% aluminum (K = kaolinite, Q = Quartz, I = illite, M = Mullite and Al = aluminum); (1) before heat treatment and (2) heat treated at 1,250˚C.

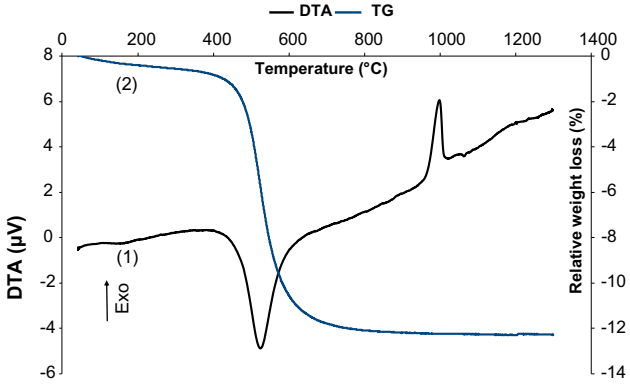

Fig. 4. Thermal behavior (1) DTA and (2) TG curves of pure kaolin.

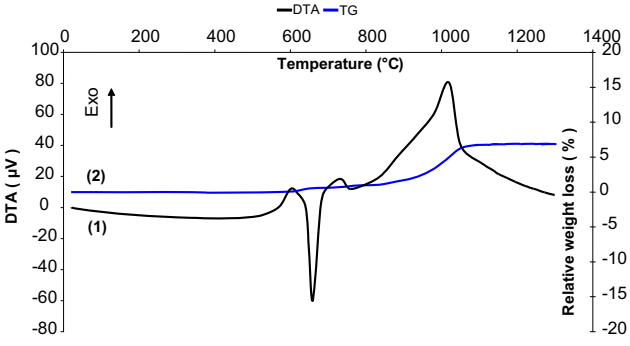

Fig. 5. Thermal behavior (1) DTA and (2) TG curves of pure aluminum.

A third stage, which is characterized by an exothermic reaction appeared at about 975˚C without any weight loss, might be attributed to the nucleus formation of spinel or mullite [23].

The DTA and TG curves of aluminum powder (Fig. 5) highlighted two areas: the first one is designated to the solid-state oxidation of aluminum at ~600˚C up to the aluminum melting at 660˚C, whereas the second is assigned to the liquid-state oxidation of aluminum from 660˚C to about 1,020˚C, as it was previously observed by other authors [24,25]. The two phenomena were associated with a weight gain of about 7% from 760 to 1,100˚C.

The addition of aluminum powder to the clay slightly modified its thermal behavior as it could be seen on the DTA–TG curves of the mixture (kaolin/10 wt.% aluminum) as shown in Fig. 6; the liquid-state oxidation field of aluminum was reduced to its melting point. This exothermic effect was associated to a slight weight gain which could be attributed to an increase of the aluminum oxidation rate.

3.2. Characterization of the ceramic supports

For the development of high-quality cermet supports, mechanical properties and hydraulic permeability are of a major importance.

3.2.1. Mechanical strength

For practical applications of the ceramic membranes, mechanical strength should be as high as possible. For the tubular configurations elaborated in this work, the mechanical resistance test was performed using the three points bending strength to control the resistance of the support elaborated with different wt.% aluminum and sintered at 1,250˚C for 1 h. The bending strength of the support samples is shown in

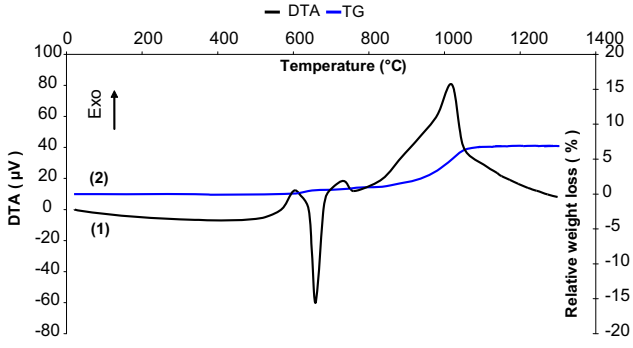

Fig. 6. Thermal behavior (1) DTA and (2) TG curves of mixture kaolin/10 wt.% aluminum.

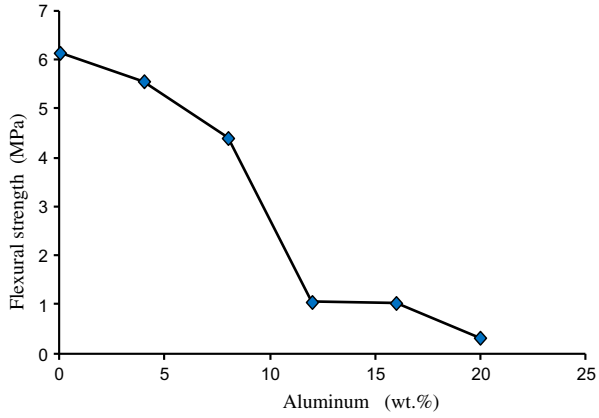

Fig. 7. Flexural strength of the samples: tubular configurations.

Fig. 7. It can be seen that the bending strength decreases slightly with the increase of the metal amounts from 0 to 8 wt.%, but then significantly between 8 and 12 wt.%, and reaches less then 1 MPa in the range of 16–20 wt.% of precursor aluminum. This can be explained by the increase of H_2 gas formation creating foams from the dissolution of aluminum in water-based suspensions which promotes the fragility of the ceramic supports. Contrary to the results found in the case of tubular supports, the addition of aluminum powder to the clay without water strongly modified its mechanical behavior as it could be seen in Fig. 8. The tensile strength gradually increases with the variation of the percentage of aluminum; the best compression resistance is obtained for 4 wt.% of metal doped in the kaolinitic matrix.

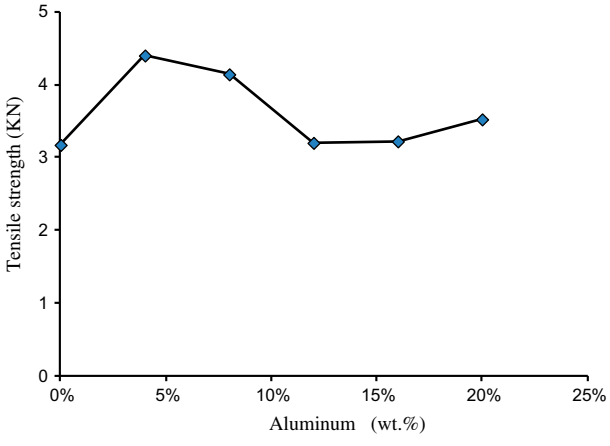

Fig. 8. Tensile strength of the samples: flat configurations.

3.2.2. Water permeability

To evaluate the performance and the presence of defects in the interior portions of the two kinds of ceramic supports, water flux characterization was used. It is always a key factor in membrane applications, as it allows the treatment of higher amounts of liquid at lower costs. The water flux for different samples made from tubular and flat configurations are presented in Figs. 9 and 10, respectively.

For tubular samples (l = 150 mm, o.d = 14 mm, and i.d = 10 mm), the membrane permeability can be determined using the variation of the water flux with the TMP. The pure water permeability for the prepared supports with different wt.% of aluminum sintered at 1,250˚C for 1 h is shown in Fig. 9. The supports elaborated with different wt.% of aluminum in the range of 4–20% sintered at 1,250˚C shows high permeability, but low bending strength as it is seen in Fig. 7. It cannot offer sufficient mechanical strength for a system to withstand pressure gradients imposed during various practical applications. It is clear that higher ratios of aluminum doped in the kaolinitic matrix make the filters more permeable due to the increase of the mean pore size. The reason for this behavior is the increase of H_2 gas formation created from the dissolution of aluminum in water.

As obtained in water permeation results with tubular configurations, the flat ones show that increasing the metal content leads to more permeable cermet supports for membranes. From Fig. 10, it is clear that an increase of aluminum ratios to the kaolinitic substance causes a higher permeation and vice versa. The reason for this behavior is probably that the exothermic oxidation reaction of aluminum would provide energy for germination of α-alumina phase which then reacts with metakaolin to form the porous mullite phase; this reaction gives rise to bigger voids and pores for flat supports prepared by dry pressing. Ebadzadeh [24] reported similar results for producing mullite–zirconia composite by reactive sintering of zircon and aluminum powder, and observed that porosity was due to aluminum oxidation.

3.2.3. Open porosity

Fig. 11 shows the influence of introduced aluminum in the open porosity of the two support shapes sintered at 1,250˚C for 1 h. The porosity increases with the increment of metal ratios for the two configurations. Porous texture in the tubular ceramic supports can be regulated by aluminum addition on the kaolinitic matrix which can dissociate in water and release a great deal of H_2 gas responsible for the

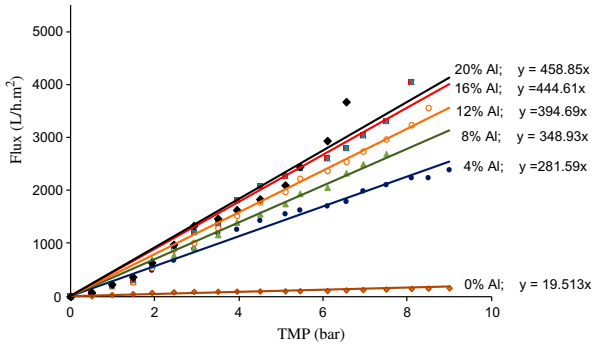

Fig. 9. The variation of flux values vs. pressure for tubular configurations.

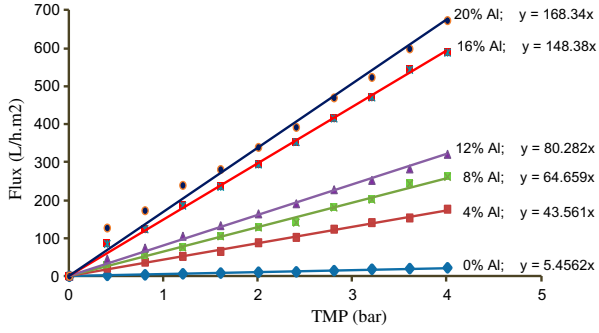

Fig. 10. The variation of flux values vs. pressure for flat configurations.

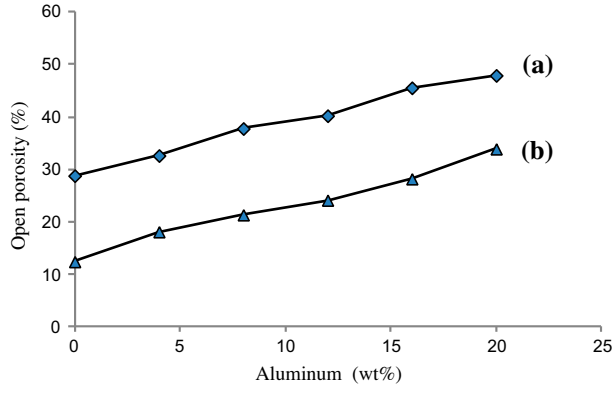

Fig. 11. The impact of the content of aluminum on the open porosity of the prepared ceramic supports sintered at 1,250°C for 1 h: (a) tubular configurations and (b) flat configurations.

formation of pores. It can be seen from the Fig. 11(a) that the open porosity increases gradually with the increasing amounts of metal and reaches about 48% from the mixture with 20 wt.% of precursor aluminum. A high porosity of 34% is obtained for the flat ceramic support derived from the mixture with 20 wt.% of metal (Fig. 11(b)). This can be due to bigger voids and pores created during the exothermic oxidation reaction of aluminum [24]. Consequently, the introduction of enough aluminum to the kaolinitic substance increases the porosity of the support.

4. Conclusions

Elaboration and characterization of two different shapes of cermet membrane supports by kaolin and aluminum powder mixtures were investigated. Tubular porous supports have been obtained by an extrusion method, whereas flat ones have been produced by dry molding. Mechanical properties, water permeabilities, and open porosities could be varied by different amounts of metal precursor. The open porosity and the pure water permeability of the tubular support sintered at 1,250°C for 1 h increase from 28.8 to 47.9% and 19.5 to 458.8 L h^{-1} m^{-2} bar^{-1}, respectively, with the addition of aluminum from 0 to 20 wt.%, whereas the mechanical strength of the sample decreases and reaches less then 1 MPa in the range of 16–20 wt.% of precursor metal. In the case of the flat support sintered at 1,250°C for 1 h, the increasing of the metal ratio in kaolin matrix from 0 to 20 wt.% has led to more permeable cermet support with open porosity ranging from 12.4 to 34% and has enhanced the mechanical strength for sample with 4% of precursor aluminum.

This investigation provides opportunities to develop ceramic supports with controllable permeability and high strength for high performance membranes.

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