

# ELABORATION AND PROPERTIES OF FLY ASH BASED MICROFILTRATION MEMBRANE SUPPORT

*Barbora THOMASOVÁ, Jan THOMAS, Lucie GEMBALOVÁ, Jiří MALÍŠ*

*Institute of Clean Technologies of Extraction and Utilization of Energy Resources, Faculty of Mining and Geology VŠB-Technical University of Ostrava, 17. listopadu 2172/15, Ostrava – Poruba, 708 00 Czech Republic*

*E-mail: [barbora.thomasova@vsb.cz](mailto:barbora.thomasova@vsb.cz)*

## ABSTRACT

The main aim of this work was to prepare a ceramic membrane support applied directly to microfiltration of industrial wastewater using a simple and cheap method. Microfiltration (MF) supports were prepared using fly ash as a dominant material and by addition of natural inorganic materials kaolin and claystone. These powders were mixed with alkali solution in order to prepare paste suitable for extrusion. The extruded tubes dried at room temperature and sintered at 1000°C showed great chemical resistance. Their morphology was examined by scanning electron microscope (SEM) and showed a homogeneous porous structure without any cracks. The average pore size distribution of the tubes was about 2 µm and pore volume was 33%. Fabricated MF membrane supports were tested using the cross-flow microfiltration process. Results with distilled water showed permeability of 680 l/h m<sup>2</sup> bar that is comparable with commercial ones.

**Keywords:** Ceramic membrane; supports; fly ash; microfiltration

## 1 INTRODUCTION

Ceramic membranes have been widely used in many industrial fields due to their significant advantages such as excellent thermal, chemical and mechanical resistance [[1]-[3]]. Ceramic membranes for the purpose of wastewater treatment belong to the oxide ceramic membranes that are mainly made of Al, Si, Ti or Zr oxides, and silicon carbide [[3]]. Membranes made of these materials exhibit excellent properties in separation of various components from wastewater from colloidal to simple molecules in dependence on active separation layers. Despite the above benefits, their wide application is limited due to their high costs of both starting materials and the sintering process [[4]]. In recent years, many researchers have focused on the development of new and cheaper ceramic membranes made of natural or waste materials [[5]-[7]]. However, most of them use organic reagents and preparation intensive process to create porous structure suitable for filtration.

In this work, we prepared porous ceramic support made of easily available materials, cheap reagents and using a simple method. Fly ash as a coal combustion by-product and natural materials such as kaolin and claystone powders were chosen as input materials in this work. Geopolymerization process described by Davidovits [[8]] using alkaline activation of aluminosilicates, the main component of materials used, enabled us to synthesise a cheap porous structure suitable for microfiltration usage. The processed tubular ceramic MF membrane support was characterized. Microfiltration tests were performed with distilled water on a lab-scale filtration unit and the results were compared with commercial MF membranes.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Chemical composition

The main constituent of the powder mixture used in this work was fly ash. Kaolin was used as traditional plastic material in ceramic production. The last powder used in the mixture was refractory claystone with its excellent thermal stability and high content of Al<sub>2</sub>O<sub>3</sub> and plastic binding ability in ceramics. The chemical compositions of powders were determined using X-ray fluorescence spectrometry (Spectro XEPOS, Germany).

The average composition of the powder input materials determined by XRFS is in Table 1. It is clear that SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the major components (80 - 95 %) of all powder samples.

**Tab. 1.: Chemical composition of fly ash, kaolin and claystone**

	Chemical composition of input materials (wt %)										
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	L.O.I.
Fly ash	0.50	1.87	26.1	54.2	0.50	0.25	3.36	2.63	1.13	6.82	2.03
Kaolin	<0.03	0.27	33.2	50.1	0.09	0.05	1.11	0.26	0.23	0.81	13.45
Claystone	0.03	0.12	41.9	53.4	0.08	0.02	0.67	0.07	1.93	1.11	0.09

High content of Al and Si ions in raw samples made the mixture suitable for geopolymerization process described by Davidovits [[8]]. During this process reorganization (destruction) of solid aluminosilicates oxides due to attack of alkali ions occurs, consequently complicated process including precipitation, gel formation, polymerization, hardening and new material formation takes place.

## 2.2 Preparation of support

Input materials were mixed in various ratios to get plastic mould suitable for extrusion. For support preparation from series of experiments, we chose the volume ratio 5/4/1 (fly ash/kaolin/claystone). The powdery solid was mixed with NaOH solution to produce a workable and mouldable paste suitable for extrusion. The volume of alkali components formed by NaOH plays a major role in the surface and structural changes in geopolymeric process of formatting of new material. Tubular shape supports of 500 mm length and of diameter 25 mm (Fig. 1) were extruded using a lab-scale extruder. Technology of drying and sintering has to be conducted to provide conditions for obtaining stable mechanical properties of the geopolymeric membrane.

**Figure 1. Image of sintered MF fly ash based membrane support**

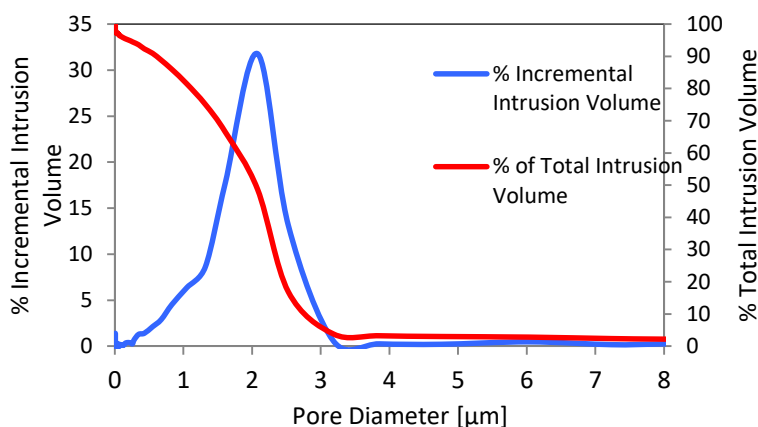
It is necessary to prevent forming of surface and inner tensions caused by quick changes in temperature of sintering. This can lead in forming of surface cracks and poor pressure durability. Therefore, the final sintering temperature was fixed at 1000°C, for 2 hours and with temperature rise of 3°C/min.

## 3 RESULTS AND DISCUSSION

### 3.1 Support characterization

#### Mercury porosimetry

Mercury (Hg) porosimetry is the basic characterization technique for permeability study and therefore was used to describe the porosity and pore size distribution of the ceramic support. Measurements were performed using the mercury porosimeter Autopore IV 9500 (Micromeritics, USA). Fig. 2. shows the pore size distribution of the fly ash based support. The median pore diameter of the support was 2.1 µm with an open porosity of 33%.

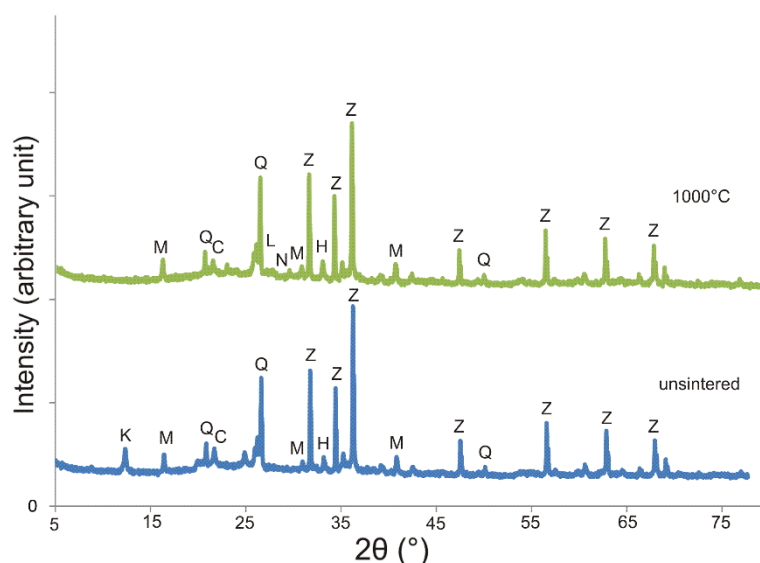


**Figure 2. Pore size distribution of the fly ash based support**

Curve of pore size distribution is almost (mono) modal showing the pore size distribution from 0.2 to 3.2  $\mu\text{m}$  with peak maximum at 2.1  $\mu\text{m}$ . MF membranes should have a pore size from 0.1 – 10  $\mu\text{m}$  and our results meet this requirement well.

### Phase identification

Phase identification was determined using an X-ray diffraction (Bruker Advance D8). XRD data for the sintered and unsintered sample are shown in Fig. 3. Semiquantitative composition of input materials was determined by the standard ZnO (Zincite) addition. In unsintered sample, the major phase was amorphous (49 %). The major crystalline phases were in the following order: mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), quartz ( $\text{SiO}_2$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). After sintering, the sample became more amorphous (55%), kaolinite transformed to mullite (silicate with isolated  $\text{SiO}_4$  tetrahedrons) whose content increased, and other silicate phases – tectosilicates (tetrahedral bounds to a spatial network) nepheline and labradorite were identified. In addition, the content of cristobalite (high temperature form of  $\text{SiO}_2$ ) increased. These changes led to creation of a solid porous structure.



**Figure 3. XRD data for unsintered and sintered support. Quartz (Q), Zincite (Z), Mullite (M), Cristobalite (C), Hematite (H), Kaolinite (K), Nepheline (N)**

### Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) images of inner profile of extruded tube before and after sintering are depicted in Fig. 4. SEM images were taken with Scanning Electron Microscope FEI Quanta FEG equipped with electron backscatter diffraction detector (EBSD). In Fig. 4 a) are visible ball shaped grains typical for fly ashes ideal for the preparation of ceramic membrane. After sintering at 1000°C the individual grains melted and become fused to one another forming a porous structure (Fig. 4 b).

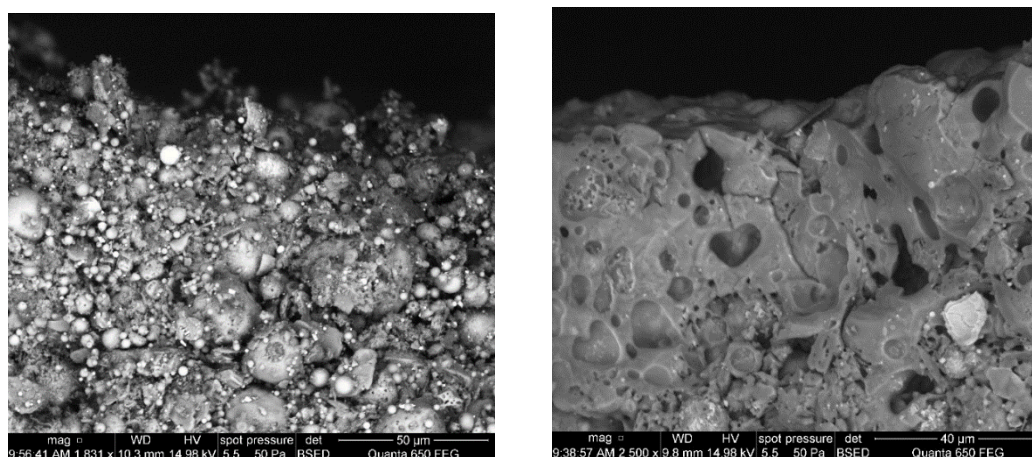


Figure 4. Inner profile of the extruded tube before a) and after sintering b)

### Chemical resistance

One of the main advantage of ceramic supports and membranes is their resistance to acidic and alkaline solution. To test the chemical stability of prepared supports, acidic and alkaline solution of pH 2 to 14 were prepared using  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  reagents. The weight loss was negligible (max 0.12%) when samples were exposed to solutions of pH 4 to pH 12 for 7 days at laboratory temperature ( $20^\circ\text{C}$ ). The weight loss of sample immersed in pH 2 solution, was 1.88% and at pH 14 it was 0.87% after 7 days of exposition. These results correspond to the chemical resistance experiments performed by Jedidi [[6]], where weight lost in the acid and alkaline solution did not exceed 2%. Results showed that the tubes should be exposed to very harsh chemical environment with negligible weight loss.

### 3.2 Determination of membrane permeability

The principle of the cross-flow filtration is shown in Fig. 5. The fluid is separated into two streams – the permeate, which is depleted of the rejected particles by filtration through the surface -  $A$  ( $\text{m}^2$ ) of the membrane, and – the concentrate, which is enriched in those particles.

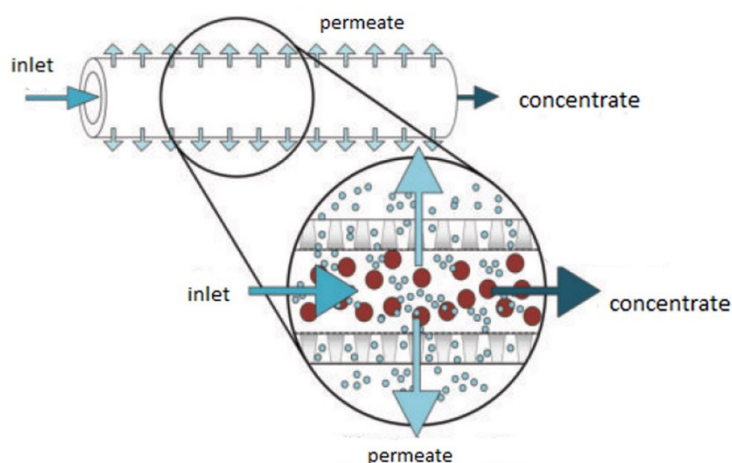
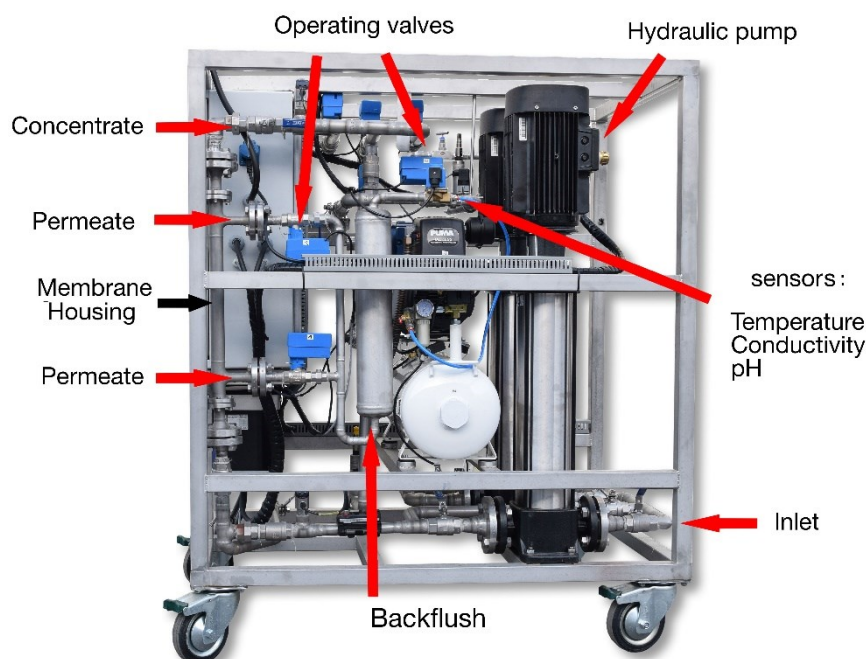


Figure 5. Principle of cross-flow filtration

Crossflow microfiltration tests were performed using a laboratory unit (Fig. 6) supplied by ASIO TECH spol. s r. o. The unit is able to operate at flow rates of 600 – 1400 l/h and for pressures adjusted up to 20 bar for each flow by control valves. The inlet, retentate (concentrate) and filtrate (permeate) pressure are measured automatically as well as physical parameters as temperature, electrical conductivity and pH are recorded.



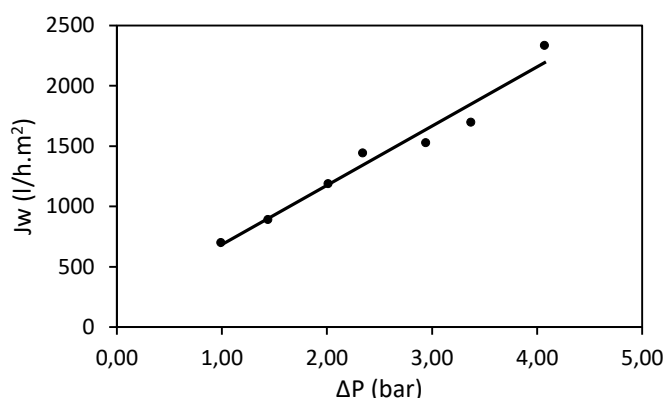
**Figure 6. Filtration laboratory unit**

In membrane permeability test the distilled water was used. The water flow rate  $Q$  (l/h) was fixed at 600 l/h and the inlet pressure was gradually increased up to 4 bars. Membrane permeability  $L_p$  (l/h.m<sup>2</sup>.bar) can be determined using the variation of the water flux  $J_w$  (l/h.m<sup>2</sup>) with the transmembrane pressure  $\Delta P$  (bar) following the Darcy's law:

$$J_w = L_p \cdot \Delta P \quad (1)$$

$$L_p = Q/A \quad (2)$$

where  $\Delta P = [(P_{\text{inlet}} + P_{\text{outlet}})/2 - P_f]$ ;  $P_{\text{inlet}}$  = inlet pressure;  $P_{\text{outlet}}$  = outlet pressure;  $P_f$  = filtrate pressure



**Figure 7. Water fluxes versus working pressure**

It can be seen that the water flux increase linearly with increasing applied pressure (Fig. 7.) indicating that for all the performed runs, the membrane recovers its initial permeability. The membrane permeability ( $L_p$ ) was found to be 680 l/h m<sup>2</sup> bar. The same linear dependency and comparable permeability (300 – 900 l/h m<sup>2</sup>) bar was found when commercial TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> MF membranes with 0.45-1.4 μm pore size were tested under the same conditions. This shows that the produced membrane can be used for microfiltration purposes.



#### 4 CONCLUSION

New ceramic fly ash based microfiltration membrane support have been prepared by geopolymerization process using NaOH solution as alkaline activator. Extruded one channel tubular tubes were dried and sintered under appropriate conditions in order to create porous structure suitable for microfiltration. Membrane supports characterisation was performed. It was found out that after sintering at 1000°C amorphous phase was dominant phase detected and porous structure was formed. The obtained membrane support was defect free with mean pore diameter of 2.1  $\mu\text{m}$  and porosity of 33% and showed great chemical resistance with negligible weight loss < 2% after 7 days of treatment under pH 2-14. Permeability of membrane support was tested with distilled water at lab-scale filtration unit with transmembrane fluxes from 1 to 4 bar and flow rate fixed at 600 l/h. Permeability obtained (680 l/h  $\text{m}^2$  bar) was comparable with commercial MF membranes made of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ .

These experimental results show that coal fly ash is an appropriate material for the development of MF membrane supports which could be applied directly without any other modification especially in the industrial wastewater treatment.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] DILAVER, M., S. M. HOCAOGLU, G. SOYDEMIR, M. DURSUN, B. KESKINLER, I. KOYUNCU and M. AGTAS. Hot wastewater recovery by using ceramic membrane ultrafiltration and its reusability in textile industry. *Journal of Cleaner Production*. 2018, 171, pp. 220-233. DOI: [10.1016/j.jclepro.2017.10.015](https://doi.org/10.1016/j.jclepro.2017.10.015)
- [2] SONDHII, R., R. BHAVE, and G. JUNG. Applications and benefits of ceramic membranes. *Membrane Technology*. 2003, 11, pp. 5-8, DOI: [10.1016/S0958-2118\(03\)11016-6](https://doi.org/10.1016/S0958-2118(03)11016-6)
- [3] SAMAEI, M., S. GATO-TRINIDAD and A. ALTAEI. The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – A review. *Separation and Purification Technology*. 2018, 200 pp. 198-220. DOI: [10.1016/j.seppur.2018.02.041](https://doi.org/10.1016/j.seppur.2018.02.041)
- [4] DONG, Y., J. ZHOU, B. LIN, Y. WANG, S. WANG, L. MIAO, Y. LANG, X. LIU and G. MENG. Reaction-sintered porous mineral-based mullite ceramic membrane supports made from recycled materials. *Journal of Hazardous Materials*. 2009, 172(1), pp. 180-186. DOI: [10.1016/j.jhazmat.2009.06.148](https://doi.org/10.1016/j.jhazmat.2009.06.148)
- [5] FANG, J., G. QUIN, W. WEI and X. ZHAO. Preparation and characterization of tubular supported ceramic microfiltration membranes from fly ash. *Separation and purification technology*. 2011, 80(3), pp. 585-591. DOI: [10.1016/j.seppur.2011.06.014](https://doi.org/10.1016/j.seppur.2011.06.014)
- [6] JEDIDI, I., S. KHEMAKHEM, A. LARBOT and R. B. AMAR. Elaboration and characterisation of fly ash based mineral supports for microfiltration and ultrafiltration membranes. *Ceramics international*. 2009, 35(7), pp. 2747-2753. DOI: [10.1016/j.ceramint.2009.03.021](https://doi.org/10.1016/j.ceramint.2009.03.021)
- [7] ALMANDOZ, M.C., C. L. PAGLIERO, N. A. OCHOA and J. MARCHESE, Composite ceramic membranes from natural aluminosilicates for microfiltration applications. *Ceramics International*. 2015, 41(4), pp. 5621–5633. DOI: [10.1016/j.ceramint.2014.12.144](https://doi.org/10.1016/j.ceramint.2014.12.144)
- [8] DAVIDOVITS, J. *Geopolymer Chemistry and Application*. 4<sup>th</sup> edition. France: Published by Institut Geopolymere. 2015. ISBN 9782951482098.