# STUDY ON THE PREPARATION OF CERAMIC MEMBRANES BASED ON NATURAL AND WASTE MATERIALS

Albena Yoleva[1], Stoyan Djambazov[1], Sibel Sabrieva[1], Adriana Gigova[2]

[1]*University of Chemical Technology and Metallurgy*
*8 Kliment Ohridsky, 1756 Sofia, Bulgaria,*
*E-mail: djam@uctm.edu*
[2] *Institute of Electrochemistry and Energy Systems "Acad. Evgeni Budevski"*
*Bulgarian Academy of Sciences*
*Bul. Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria*

*Received 16 October 2019*
*Accepted 10 January 2020*

## ABSTRACT

*The production of low cost ceramic membranes has been studied by many researchers using a variety of natural raw materials such as clays, kaolins, limestones, dolomites, zeolites, diatomites and various kinds of wastes such as fly ash, sawdust, sewage sludge, bagasse, waste glass, ceramic scrap, etc., modifying the membranes microstructure with the aim to improve their surface porosity, pore size, pore distribution and mechanical strength. Compositions of ceramic membranes containing halloysite clay, limestone and waste diatomite from the brewery industry are prepared. The change of the ceramic membranes properties varying the presence of halloysite clay and diatomite is followed. The ceramic membranes studied are prepared by dry pressing at 50 MPa and sintering at 1100°C within 2 h. The water absorption, the apparent density, the apparent porosity, the mechanical bending strength and the shrinkage of the ceramic membranes obtained are determined. The water absorption and the apparent porosity increase, while the apparent density and the mechanical bending strength decrease with an increase of the waste diatomite content and a decrease of halloysite clay presence in the ceramic membrane compositions. XRD and SEM are used to identify the phase composition and the microstructure. The average pore size of the ceramic membranes studied is determined by mercury porosimetry.*

*Keywords: halloysite clay, limestone, waste diatomite, apparent porosity, bending strength.*

## INTRODUCTION

Microfiltration is a membrane process widely used for purification of water and other liquid media in food, pharmaceutical and other industries. Ceramic membranes are the preferred class of macroporous membranes used for microfiltration and nanofiltration in cases requiring chemical and thermal resistance. The properties of the ceramic membranes are mainly determined by their composition, the pore-former content and the sintering temperature. The use of natural raw and waste materials is certainly preferable than industrial chemicals due to their lower cost and the environmental impact obtained. Recently, the development of low cost ceramic membranes based on natural raw materials such as kaolin, clay, zeolite, limestone, dolomite, feldspar, quartz and other appear an efficient solution of purification of water and other liquid media at a low cost [1 - 7]. Various kinds of wastes such as fly ash, sewage sludge, bagasse, waste glass, ceramic scrap, etc., modifying the membranes microstructure with the aim to improve their surface porosity, pore size, pore distribution and mechanical strength are used for ceramic membrane production. Diatomite is used in the brewing industry in the course of the final product filtration to improve its brightness. Hence, the breweries waste sludge contains diatomite material that is lightweight and can serve as a pore-forming additive to ceramic membranes. The diatomite is a non-metallic, soft, friable, fine-grained, and siliceous sedimentary rock that can be easily crumbled into a white to off-white powder. This powder is granular, and very light due to its high porosity. The diatomite contains fine pores, cavites and chanels and because of that it can separate the very fine particles that otherwise pass or clog the filter net [8 - 16].

The purpose of the present paper refers to the preparation and characterization of ceramic membranes containing halloysite clay, limestone and waste diatomite from the brewery industry.

## EXPERIMENTAL

### Methods of the raw materials and the sintered ceramic membranes characterization

The following methods were used to characterize the raw materials and the sintered ceramic membranes:

The chemical analyses was performed by ICP-AES;

The phase compositions of the raw materials and the sintered ceramic samples were identified by X-ray diffraction (XRD, DRON 3M, Co-$K_a$ radiation);

The pore size distribution was measured by mercury porosimetry (Micromeritics, Model Autopore 9200);

The microstructure of the sample surfaces was observed using a SEM (Philips SEM 525M/ EDAX9900);

The properties of the sintered ceramic membranes such as shrinkage, water absorption, an apparent density, an apparent porosity were determined by standard methods applicable to ceramic materials including the Archimedes method;

The mechanical bending strength of the sintered samples of a rectangular shape was measured by a three-point bending test.

### Natural and waste raw materials used

Halloysite clay and limestone from Southeastern Bulgaria were the natural raw materials used in this experimental work. Waste diatomite from the brewery industry was used as a pore former in the ceramic membranes prepared. The chemical composition of the halloysite clay referred to: $Al_2O_3$ (31,29 wt.%), $SiO_2$ (51,43 wt.%), $Fe_2O_3$ (2,22 wt.%) CaO (2,34 wt.%), MgO (0,37 wt.%), $K_2O$ (1,17 wt.%), $Na_2O$ (0,76wt.%), $TiO_2$ (0,42 wt.%), (LOI 9,43 wt.%). The clay was found basic (31,29 wt.% $Al_2O_3$) with an average content of coloring oxides and a low content of alkaline and earth-alkaline oxides. The mineral composition of the halloysite clay is presented in Fig. 1. The clay contained mainly the plastic component halloysite. The nonplastic component potassium feldspar was found present in small amounts. The clay impurity referred to calcite. The limestone was of purity higher than 99.00%. Its chemical composition was as follows: CaO (54,75 wt.%), MgO (0,24 wt.%), $Al_2O_3$ (0,28 wt.%), $SiO_2$ (1,20 wt.%), $Fe_2O_3$ (0,13 wt.%) $K_2O$ (0,05 wt.%), $Na_2O$ (0,05wt.%), $TiO_2$ (0,02 wt.%), (LOI 42,76 wt.%). The XRD of limestone is shown in Fig. 2. Calcite was the only crystal phase present in the limestone. The chemical composition of the waste diatomite from the brewing industry referred to: $SiO_2$ (70,09 wt.%), $Al_2O_3$ (4,24 wt.%), $Fe_2O_3$ (1,74 wt.%) CaO (0,54 wt.%), MgO (0,42 wt.%), $K_2O$ (0,54 wt.%), $Na_2O$ (0,47 wt.%), $TiO_2$ (0,23 wt.%), (LOI 20,62 wt.%). The XRD data of the waste diatomite is presented in Fig. 3. $SiO_2$ (70,09 %) was the main component of the dried brewing waste sludge. The XRD patterns indicated the presence of cristobalite as a crystalline phase together with an amorphous phase.

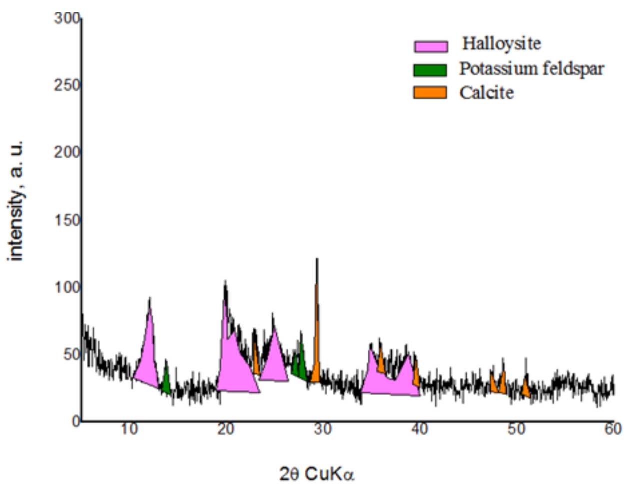

Fig. 1. XRD of halloysite clay.

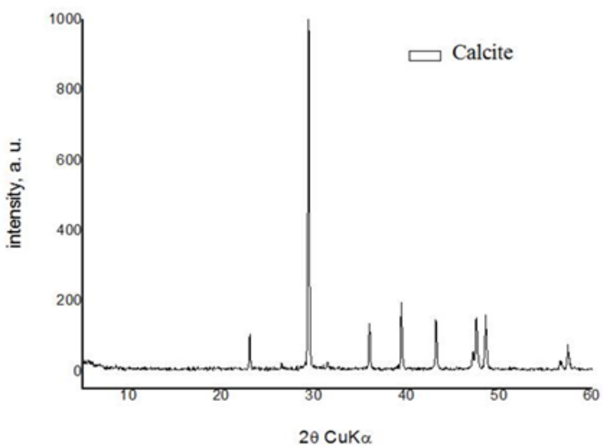

Fig. 2. XRD of limestone.

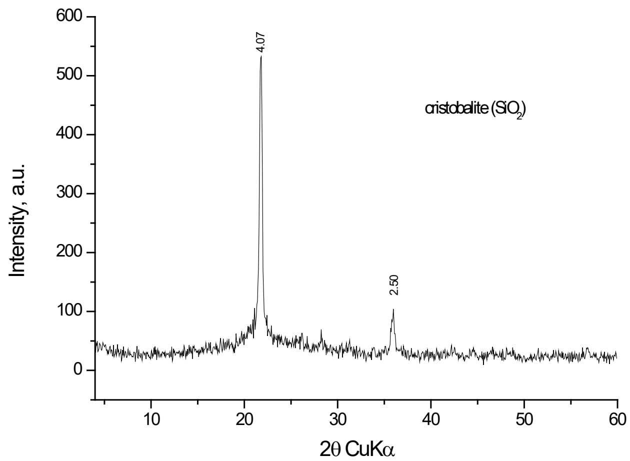

Fig. 3. XRD of waste diatomite.

**Preparation of the ceramic membranes**

The halloysite clay was crushed and wet grinded obtaining slurry which could pass through a 63 micron sieve. It was dried at 105°C. The limestone was dry grinded to a powder of a particle size less than 50 μm. The waste diatomite sludge was incorporated into the ceramic samples after drying at 105°C. The dried diatomite powder was of a particle size less than 63 μm. Four ceramic membrane compositions (shown in Table 1) having an identical content of limestone, but different amounts of halloysite clay and waste diatomite were formed by dry pressing at a pressure of 50 MPa in the form of a 3 cm x 0.4 cm rectangular samples. The initial dry homogenized batches were prepared from the dried raw materials, and fired within 2 h at 1100°C.

**RESULTS AND DISCUSSION**

The physical-mechanical properties of the ceramic samples prepared referring to their shrinkage, water absorption, apparent density, apparent porosity and mechanical bending strength are summarized in Table 2.

The apparent porosity decreases, while the mechanical bending strength increases increasing the amount of clay and decreasing that of the waste diatomite. The pore size distribution curve of composition 3 is shown in Fig. 4. The average pore size in the ceramic membrane containing 60 wt.% of halloysite clay, 20 wt.% of limestone and 20 wt.% of waste diatomite refers to 2,85 μm. The total porosity determined by the Archimed methods and mercury porosimetry amounts to 50,05 %. The phase composition of the same sample after sintering at 1100°C is shown in Fig. 5. It shows the presence of anorthite and wollastonite

Table 1. Ceramic membranes compositions.

| Raw materials, wt.% / Compositions | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Halloysite clay | 40 | 50 | 60 | 70 |
| Limestone | 20 | 20 | 20 | 20 |
| Waste diatomite | 40 | 30 | 20 | 10 |

Table 2. Properties of sintered at 1100°C ceramic membranes.

| Properties / Compositions | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Shrinkage, % | 1,0 | 1,0 | 1,3 | 2,5 |
| Water absorption, % | 42,5 | 40,5 | 38,5 | 32,0 |
| Apparent density, g/cm$^3$ | 1,27 | 1,29 | 1,3 | 1,47 |
| Apparent porosity, % | 54,00 | 52,25 | 50,05 | 47,00 |
| Mechanical bending strength, MPa | 11 | 12 | 13 | 16 |

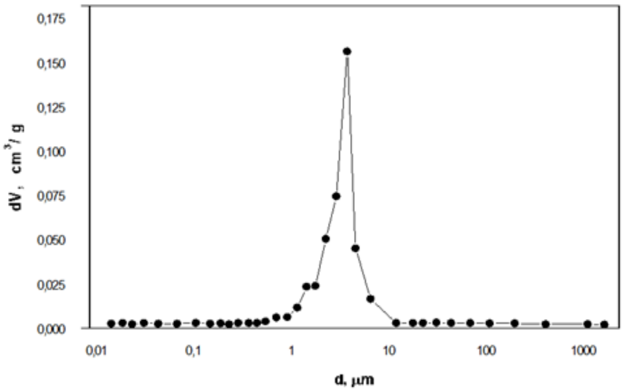


Fig. 4. Pore size distribution of sintered at 1100°C ceramic membrane with composition 3.

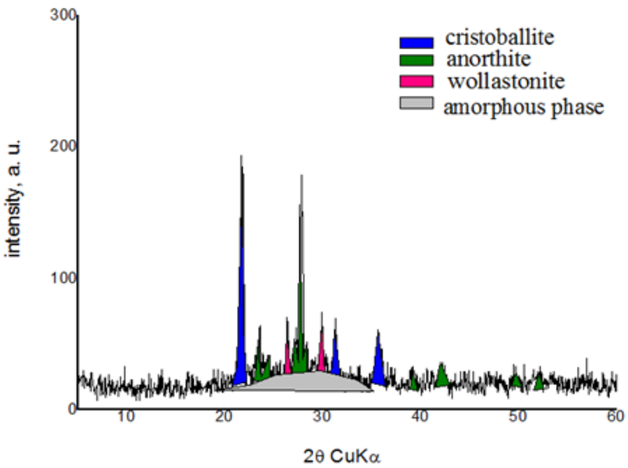


Fig. 5. XRD of sintered at 1100°C ceramic membrane with composition 3.

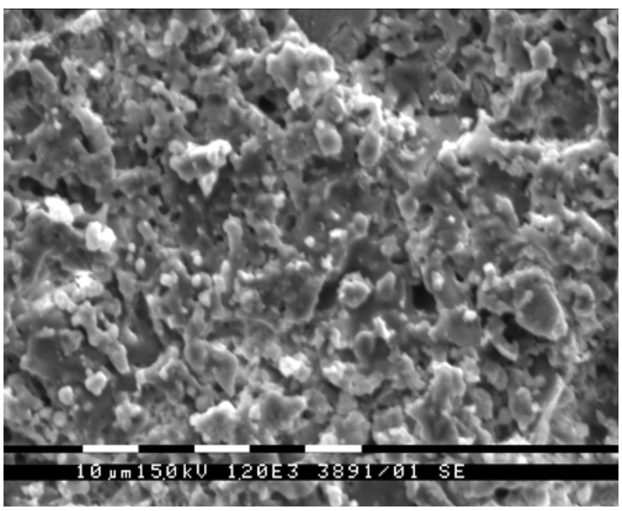


Fig. 6. SEM of sintered at 1100°C ceramic membrane with composition 3.

as well as that of an amorphous phase, whose amount changes with a variation of the sample composition. The SEM image of sample considered is presented in Fig. 6. The microstructure of the ceramic membrane containing 60 wt.% of halloysite clay, 20 wt.% of limestone and 20 wt.% of the waste diatomite is porous with predominantly homogeneously distributed pores of a size less than 10 µm.

## CONCLUSIONS

The preparation of ceramic membranes based on natural material (halloysite clay and limestone) and a waste (diatomite from the brewery industry) is reported in this work. The ceramic membranes are obtained by dry pressing at 50 MPa. Rectangular samples of 3 cm x 0.4 cm were formed and subsequently sintered at 1100°C within 2 h. The change of the properties of the sintered ceramic membranes varying their composition is established. The apparent porosity of the samples decreases, while the mechanical bending strength increases by increasing the halloysite clay content and decreasing that of the diatomite. The phase composition of the ceramic membranes shows the presence of anorthite and wollastonite as well as that of an amorphous phase, whose amount changes with a variation of the composition of the ceramic samples. By using mercury porosimetry it is found that the average pore size in the ceramic membrane containing 60 wt.% of halloysite clay, 20 wt.% of limestone and 20 wt.% of waste diatomite is 2.84 µm. The apparent porosity of the same ceramic membrane composition amounts to 50.05 % measured by the Archimed's method and mercury porosimetry. It is established that ceramic membranes containing halloysite clay, limestone, and waste diatomite can be produced. The amount of the halloysite clay is recommended to be between 60 wt.% and 70 wt.%, that of limestone has to equal 20 wt.%, while that of the waste diatomite may vary between 10 wt.% and 20 wt.%. This ratio of raw materials results in the appropriate apparent porosity and the mechanical bending strength of the sintered ceramic samples which provide their use as ceramic membranes.

## REFERENCES

1. B. Ghouil, A. Harabi, F. Bouzerara, B. Boudaira, A. Guechi, M. Demir, A. Figoli, Development and characterization of tubular composite ceramic membranes using natural alumino-silicates for microfiltration applications, Mater. Characteriz., 103, 2015, 18-27.

2. S. Jana, M. Purkait, K. Mohanty, Preparation and characterization of low-cost ceramic microfiltration membranes for the removal of chromate from aqueous solutions, Appl. Clay Sci., 47, 2010, 317-324.
3. F. Bouzerara, A. Harabi, S. Condom, Porous ceramic membranes prepared from kaolin, Desalin. and Water Treatm., 12, 2009, 415-419.
4. B. Boudaira, A. Harabi, F. Bouzerara, S. Condom, Preparation and characterization of microfiltration membranes and their supports using kaolin (DD2) and $CaCO_3$, Desalin. and Water Treatm., 9, 2009, 142-148.
5. Y. Dong, S. Chen, X. Zhang, J. Yang, X. Liu, G. Meng, Fabrication and characterization of low cost tubular mineral-based ceramic membranes for microfiltration from natural zeolite, J. Membr. Sci., 281, 2006, 592-599.
6. F. Bouzerara, A. Harabi, S. Achour, A. Labrot, Porous ceramic supports for membranes prepared from kaolin and doloma mixtures, J. Europ. Cer. Soc., 26, 2006, 1663-1671.
7. S. Masmoudi, A. Larbot, H. El Feki, R. Ben Amar, Elaboration and characterization of apatite based mineral supports for microfiltration and ultrafiltration membranes, Ceram. Intern., 33, 2007, 337-344.
8. Y. Dong, X. Liu, Q. Ma, G. Meng, Preparation of cordierite-based porous ceramic micro-filtration membranes using waste fly ash as the main raw materials, J. Membr. Sci., 285, 2006, 173-181.
9. A. Harabi, A. Guechi, S. Condom, Production of supports and filtration membranes from Algerian kaolin and limestone, Proc. Engin., 33, 2012, 220-224.
10. Harabi, F. Zenikheri, B. Boudaira, F. Bouzerara, A. Guechi, L. Foughali, A new and economic approach to fabricate resistant porous membrane supports using kaolin and $CaCO_3$, J. Europ. Cer. Soc., 34, 2014, 1329-1340.
11. Y. Dong, X. Feng, X. Feng, Y. Ding, X. Liu, G. Meng, Preparation of low-cost mullite ceramics from natural bauxite and industrial waste fly ash, J. Alloys Compd., 460, 2008, 599-606.
12. Y. Dong, S. Hampshire, J. Zhou, B. Lin, Z. Ji, X. Zhang, G. Meng, Recycling of fly ash for preparing porous mullite membrane supports with titania addition, J, Hazard, Mater., 180, 2010, 173-80.
13. J. Han, E. Oh, B. Bae, I. Song, The fabrication and characterization of sintered diatomite for potential microfiltration for applications, Ceram. Intern., 39, 2013, 7641- 7648.
14. S. Fakhfakh, S. Baklouti S., Elaboration and characterisation of low cost ceramic support membrane, Adv. Appl. Ceram., 109 2010, 31-38.
15. R. Arboledas, T. Cotes, C. Martınez, S. Bueno, Influence of waste addition on the porosity of clay-based ceramic membranes, Desal. and Water Treatm., 57, 2016, 2633-2639.
16. F. Akhtar F, Y. Rehman, L. Bergström, A study of the sintering of diatomaceous earth to produce porous ceramic monoliths with bimodal porosity and high strength, Powder Technol., 201, 2010, 253-257.