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PREPARATION AND CHARACTERIZATION OF CERAMIC MEMBRANES ON THE BASE OF HALLOYSITE CLAY AND LIMESTONE

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ABSTRACT

The development of ceramic membranes based on natural raw materials such as kaolins, clays, zeolites, limestones, dolomites, feldspars, quartzs and others appears an efficient solution to purification of water at a low cost. The ceramic membranes are prepared in the form of disks of a size of 3,0 cm x 0,4 cm by dry pressing of a homogenized batch from halloysite clay and limestone of different quantities at pressure of 50 MPa. They are fired for 2 h at 1100^{o}C. The properties of the sintered ceramic membranes such as shrinkage, water absorption, an apparent density, an apparent porosity and a mechanical bending strength are determined by standard methods. Mercury porosimetry is used to determine the pore size distribution and the average pores size. The phase composition is identified by XRD analysis. The microstructure is observed using SEM. The increase of the limestone content results in an increase of the water absorption and the apparent porosity and a decrease of the shrinkage, the apparent density and the compressive strength. The average pore size equals 2,32 μm, while the total porosity amounts to 45,00 % for the ceramic membrane containing 60 wt.% of halloysite clay and 30 wt.% of limestone. The main crystalline phases found in the sintered ceramic samples refer to anorthite ($CaO.Al_2O_3.2SiO_2$), gehlenite ($2CaO.Al_2O_3.SiO_2$), mullite ($2Al_2O_3.SiO_2$) and wollastonite ($CaO.SiO_2$).

Keywords: *ceramic membranes, halloysite clay, limestone, properties, structure.*

INTRODUCTION

The ceramic membranes are a preferred class of macroporous membranes used for microfiltration and nanofiltration where chemical and thermal resistance is required. The following features are important for the development of high-quality membranes: a pore size distribution, porosity, mechanical properties and a chemical stability. The demand for ceramic membranes has increased in recent years due to the increasing pollution of drinking water. The ceramic membranes have many advantages compared with those of the polymeric one. They refer to their high thermal and chemical stability, high pressure resistance, long lifetime, a good resistance to fouling, and an ease of cleaning [1 - 6]. The use of natural raw materials is certainly preferable than that of industrial chemicals due to their lower cost and environmental impact. The development of low-cost ceramic membranes based on natural raw materials such as kaolins, clays, zeolites, limestones, dolomites, feldspars, quartzs and others has recently appeared an efficient solution of water purification. The properties of the ceramic membranes are mainly determined by their composition, the pore-former content and the sintering temperature [7 - 13].

The investigation reported is focused on the preparation and characterization of low-cost ceramic samples from halloysite clay and limestone of different quantities aiming to determine the appropriate compositions required.

EXPERIMENTAL

Raw materials

The natural raw materials used in this experimental work referred to halloysite clay and limestone from Southeastern Bulgaria. The halloysite clay was crushed and wet grinded until the slurry could pass through a 63-micron sieve. Then the slurry was dried at 105°C. The limestone was dry grinded to a powder of a particle size of less than 50 microns. The raw materials were characterized by a chemical analysis, XRD, and DTA.

A preparation of ceramic membranes

Ceramic membrane of compositions of a varying ratio of haloysite clay and limestone were prepared. The ceramic membrane compositions are shown in Table. 1.

Halloysite clay and limestone were dry homogenized, then dry pressed at 50 MPa in the form of a 3 cm x 0.4 cm discs and fired at 1100°C for 2 h. Samples of a size of 3 cm x 3 cm were also pressed to be used for their compressive strength determination. The ceramic membranes sintered at 1100^{o}C are shown in Fig. 1. The shrinkage, the water absorption, the apparent density, the apparent porosity and the compressive strength of the fired ceramic samples were determined.

Methods for characterization of the raw materials and the fired ceramic samples

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

The chemical analysis was performed by AES-ICP;

The phase composition of the raw materials and the ceramic samples was identified by X-ray diffraction (XRD, DRON 3M, Co-K_α radiation);

The structural evolutions of halloysite and limestone powders were evaluated by DTA and (TG) analyses using STA PT1600 TG-DTA/DSC in the range of 20^{o}C -1200^{o}C at 10 ^{o}C/min;

Fig. 1. Ceramic membranes sintered at 1100^{o}C.

The total porosity and the pore size distribution were measured by mercury porosimetry (Micromeritics, Model Autopore 9200);

The microstructure of the sample surfaces was observed by 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 the standard methods for ceramic materials including the Archimedes method;

The mechanical compressive strength of the sintered samples of a size of 3 cm x 3 cm was determined via the hydraulic press test.

RESULTS AND DISCUSSION

The chemical composition of the halloysite clay is given in Table 2. The clay is determined basic (31,29 % 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. 2. The clay is mainly composed of

Table 1. Ceramic membrane compositions.

Raw materials / Compositions	0	1	2	3
Halloysite clay, %	100	90	80	70
Limestone, %		10	20	30

Table 2. Chemical composition of halloysite clay.

Oxides, wt. %	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	SiO_2	TiO_2	IL
Halloysite clay	31,29	2,34	0,37	2,22	1,17	0,76	51,43	0,42	9,43

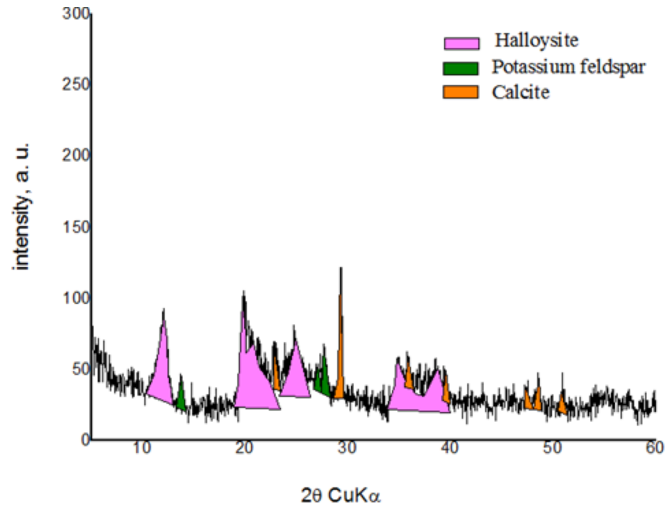

Fig. 2. XRD of halloysite clay.

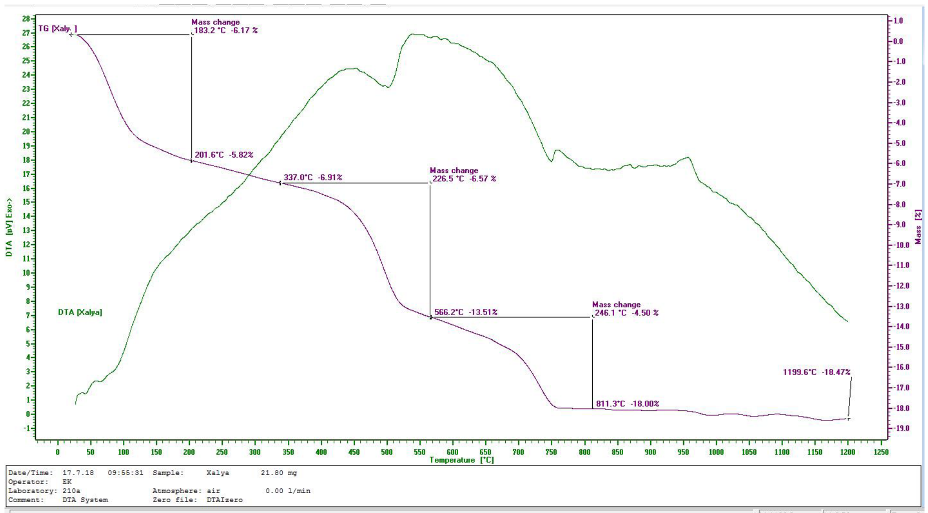

Fig. 3. DTA and TG of halloysite clay.

halloysite. It also contains a little amount of potassium feldspar. Calcite is found as an impurity. The DTA and TG results of halloysite clay are shown in Fig. 3.

Three endothermic effects are observed below 100°C, at 500°C and at 750°C. They are associated with the release of physically and chemically bound water and the destruction of the clay structure. The decomposition of the calcium carbonate contained in the clay as an impurity occurs at 750°C. There is also an exothermic reaction that occurs at about 970°C, which is associated with nucleus formation of mullite. The limestone is of a purity greater than 99.00 %. The chemical composition of the limestone is given in Table 3. The XRD of limestone is shown in Fig. 4. The DTA and TG results are shown in Fig. 5. The only crystal phase of limestone refers to the calcite.

Fig. 5 shows that there is only one endothermic peak (a mass loss of 41.80 %) in the range of 637°C - 869°C. It is observed at 840°C and is due to the thermal decomposition of $CaCO_3$ to CaO and CO_2.

Table 3. Chemical composition of limestone.

Oxides, wt. %	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	SiO_2	TiO_2	IL
Limestone	0,28	54,75	0,24	0,13	0,05	0,05	1,20	0,02	42,76

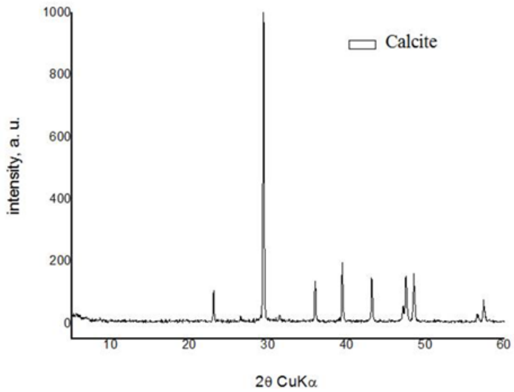

Fig. 4. XRD of limestone.

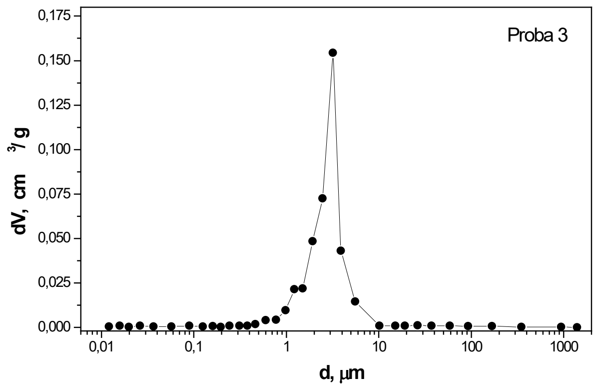

Fig. 6. Pore size distribution in ceramic membrane with composition 3 (70 wt% halloysite clay 30 wt.% limestone) sintered at 1100°C.

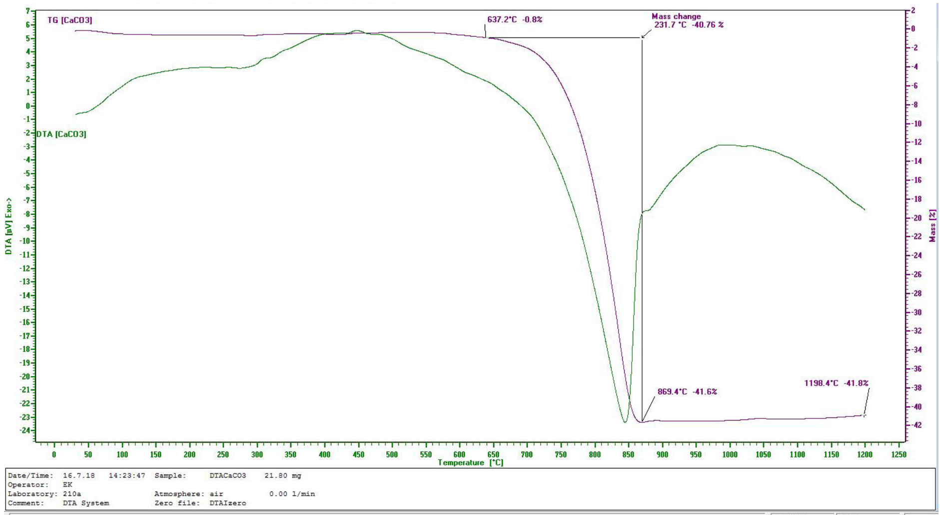

Fig. 5. DTA and TG of limestone.

The results referring to the measured properties of the ceramic membranes sintered at 1100°C are presented in Table 4. The water absorption and the apparent porosity increase with the increase of the limestone content of the ceramic membranes. The shrinkage, the apparent density and the compressive strength decrease with the increase of the limestone content. The pore size distribution curve of the ceramic membrane containing 60 wt.% of halloysite clay and 30 wt.% of limestone, sintered at 1100°C, is shown in Fig. 6. The average pore size is 2,32 μm, while the total porosity equals 45,00 %.

Figs. 7-9 show diffractograms of ceramic membranes sintered at 1100°C. They contain 10 wt. %, 20 wt. % and 30 wt. % of limestone. The main crystalline

Table 4. Properties of sintered ceramic samples.

Properties / Compositions	0	1	2	3
Shrinkage, %	8,9	4,6	3,6	3,0
Water absorption, %	13,00	22,00	25,00	30,00
Apparent density, g/cm^3	2,00	1,68	1,64	1,50
Apparent porosity, %	26,00	37,00	41,00	45,00
Compressive strength, MPa	95,0	65,0	55,0	32,0

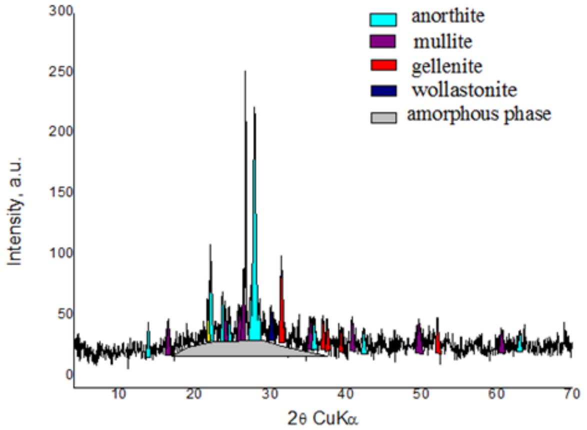

Fig. 7. XRD of a sintered at 1100°C ceramic membrane with a composition 1(90 wt.% halloysite clay and 10 wt.% limestone).

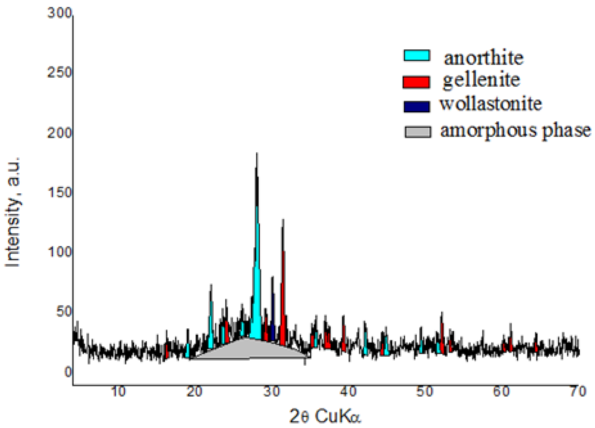

Fig. 8. XRD of a sintered at 1100°C ceramic membrane with a composition 2 (80 wt.% halloysite clay and 20 wt.% limestone).

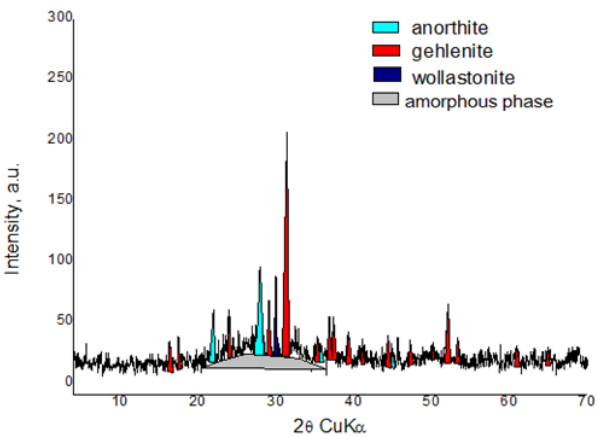

Fig. 9. XRD of a sintered at 1100°C ceramic membrane with a composition 3 (70 wt.% halloysite clay and 30 wt.% limestone).

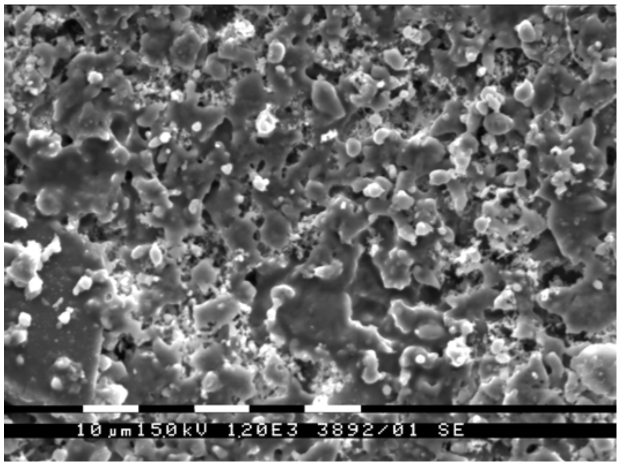

Fig. 10. SEM of a sintered ceramic membrane with composition 3 (70 wt.% halloysite clay and 30 wt.% limestone).

phases found in the sintered ceramic samples refer to anorthite ($CaO.Al_2O_3.2SiO_2$), gehlenite ($2CaO.Al_2O_3.SiO_2$), mullite ($2Al_2O_3.SiO_2$) and wollastonite ($CaO.SiO_2$). They also contain an amorphous phase. The quantity of the anorthite decreases, while those of the gehlenite and wollastonite increase with the increase of the amount of calcium carbonate.

Fig. 10 illustrates the SEM pictures of the ceramic membrane of composition 3 (70 wt. % of halloysite clay and 30 wt. % of limestone) sintered at 1100°C. A homogeneous porous structure of predominantly homogeneously distributed pores smaller than 10 μm is observed.

CONCLUSIONS

The present communication reports the preparation of ceramic membranes based on low cost natural raw materials - halloysite clay and limestone. The effect of the increase of the amount of calcium carbonate in the membrane composition on the properties of the material sintered at 1100°C is studied. It is found that the apparent porosity increases, while the compressive strength decreases with the increases of the calcium carbonate content.

It is found by mercury porosimetry that the average pore size of the ceramic membrane containing 30 wt.% of limestone equals 2.32 microns. The apparent porosity of the sample is 45 % measured by the Archimed's method and mercury porosimetry.

The phase composition of the ceramic samples determined by XRD indicates the presence of mullite, anorthite, gehlenite, wollastonite, crystobalite and an amorphous phase. The increase of the amount of calcium carbonate in ceramic membranes of composition from 1 to 3 results in a decrease of the amount of anorthite and an increase of that of gehlenite and wollastonite.

The study carried out provides the conclusion that single-layer or multilayer ceramic membranes for water microfiltration can be produced on the ground of halloysite clay and limestone. The recommended limestone content of 30 wt. % provides the required porosity and mechanical strength of the ceramic membranes prepared.

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