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Polymer inorganic- organic composites- precursors for ceramic powders and products

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Abstract. This work presents the results obtained in the researches for synthesis of new polymer composites and their use for the preparation of ceramic powders and ceramic porous products. New inorganic- organic hydrogels were prepared by the copolymerization of acrylic acid with N, N'- methylene bis acrylamide in concentrated slurries of kaoline or alumina and mixtures of them. The hydrogels were used to prepare ceramic foams by gel casting. The ceramic foams prepared from these hydrogel precursors by the burning of the polymer can be used for waste gases purification (filtration of hot gases from power plants). The hydrodynamic characteristics of new ceramic foams were also assessed.

Keywords: Polymer composite, Ceramic foams, Kaolin, alumina.

1. Introduction

A serious threat for the modern society is the continuously decreasing of environment quality, as industrial activities pose negative impact upon soil, water and air. Production of energy in power plants (especially when using fossil coals), is greatly affecting environment and implicitly the quality of life. On the other hand, the worldwide coal supply is high enough, so that in the future it will be an important source for energy production. Consequently, promoting new materials is

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mandatory in order to provide an environmentally friendly activity of the coal-based power plants.

Methods and solutions for decreasing air pollution are continuously improved, based on advanced knowledge regarding effects of the pollution agents. A great deal of interest is paid to the new, "clean" nonpolluting technologies, related to burning processes and energy production. During the last decade, there have been developed procedures and modern equipment for reducing harmful effects of emissions. Global research programs, developed to apply this kind of technologies, are focusing on decreasing the emissions according to environment legal regulations.

Ceramic foams exhibit several outstanding properties: low density, enhanced thermal stability, high permeability and porosity, low thermal conductivity and heat capacity, properties which make them useful in many economic fields. Depending on porosity degree (which might be between 50-90%), on average cell diameters (which ranged from 10 μ m to 5 mm) and on type of the cell (closed or open), with a geometry similar to that of tetrakaidecahedron, ceramic foams can be used in a wide range of engineering applications: filters and filters coupled with catalytic system for treatment of hot gaseous streams released from thermo-power stations, incineration and industrial processes, catalyst supports, biomaterial carriers, thermal insulators for furnaces and aeronautic applications, lightweight materials, etc. [1,2]

Performances of ceramic foams are strongly related to their preparation method; therefore, a wide range of processing routes has been proposed worldwide. A few methods already implemented or with good chances to be commercially applied are:

(i) Polymer replica technique (RP) (polyurethane, polyvinylchloride, cellulose, natural latex, etc.) which involves dipping a porous polymer matrix (as flexible foam is) in an aqueous suspension of mixed oxides (alumina, silica, magnesium oxide, etc.) in presence of wetting additives in order to achieve intimate impregnation [3]. Afterwards, the resulted material is exposed to a strictly controlled heating process for drying, calcinations and sintering, the polymer matrix being consequently removed by burning, the ceramic foam being formed. The main drawback of this route is the great size difference between cells located in the foam middle and at its surface (due to lack of a uniformly squeezing out); (ii) Direct foaming of an inorganic suspension, using a solvent with low boiling point, followed by thermal treatment [4]. This method provides only 70% porosity; (iii). Burning, with elimination of porogenic agents, released as a result of decomposition of various polymers: poly-methylmethacrylates or starch [5]. This method provides heterogeneous porosity; (iv). Sol-gel technique: the foam is growing simultaneously with ceramic [6,7]. The method provides a porosity degree of about 90% under wet condition. Unfortunately, contraction during drying decreases drastically porosity, down to 50%.; (v). Gel casting technique consisting of the preparation of an aqueous suspension of ceramic oxide containing gelling agents and foam additives, which is vigorously mixed. The suspension is then

poured in a mold and cooled under gel formation temperature. After that, a controlled thermal treatment is applied (drying, calcination, sintering) [8-12]. This method has several alternatives, the most attractive one being gel polymerization. This route provides both homogenous pore size distribution, up to 90% porosity degree in dry condition and outstanding mechanical and physical properties. This article was aimed at developing ceramic foams by gel casting system and to assess their capacity to be used for filtering of hot gases.

2. Experimental part

2.1. Materials

Kaolin powder (K) was purchased from the Aghires quarry (Cluj, Romania) and had the following chemical composition (in mass%): Al₂O₃ 48.75, SiO₂ 42.75, K₂O 0.65, CaO 0.98, TiO₂ 2.56, Fe₂O₃ 3.30, Na₂O 0.50 and MgO 0.74. Alumina (Al) was a commercial product from SC Alumn Tulcea and it was used as received. Acrylic acid (AA), ALDRICH, 99% was distilled under vacuum and stored in the freezer. Potassium persulfate (KPS), ACROS ORGANICS, 99%, sodium metabisulfite (MS), ACROS ORGANICS, 97% and N, N'-methylene bisacrylamide (MBA, SIGMA-ALDRICH, 99%) were used without further purification. The ammonium polyacrylate dispersant was prepared as described in [11].

2.2. Ceramic Foams preparation

The ceramic dispersions were prepared according to [11] by adding kaolin or alumina to an aqueous solution of NH₄PAA in distillate water, so that the inorganic content in the final dispersion was around 40 mass%. The concentration of the NH₄PAA dispersant was around 17 mass%. After stirring for 1h, AA, MBA and the aqueous solution of the redox initiation system (KPS/MS) were added to the reaction mixture. The AA monomer concentration was varied between 15 and 35 mass% relative to inorganic content. The concentration of the redox initiation system was [KPS]=[MS]=0.5 mass% relative to AA. The AA: MBA mass ratio was kept constant at 1% relative to AA. After 2 minutes stirring, the dispersion was cast into 10 mm diameter glass vials and purged 2–3 minutes with nitrogen to remove dissolved oxygen. The vials were sealed by septa plastics and kept at room temperature for polymerization. After 2h, the vials were broken, and the resulting green bodies were cut into small cylindrical pieces. The undried green bodies bear moisture. For this reason, they were dried for 24 h at room temperature and then at 105 °C to constant mass. The green bodies were heated at 1100°C, at atmospheric pressure with a heating rate of 10°C/min and dwelling time of 4h. The preparation scheme for obtaining ceramic foams is shown in Fig.1.



Fig. 1. Scheme for preparing ceramic foams.

Composites with K and Al at various AA concentrations in the aqueous solutions were prepared. The hydrogel nanocomposites are designated as KAl-xAA when kaolinite and alumina particles are incorporated, and as K-xAA when only kaolinite particles are incorporated, where X represents the concentrations in AA. The synthesis recipes of the nanocomposite hydrogels based on acrylic acid and kaolinite or kaolinite/alumina particles are given in Table 1.

Table 1. The synthesis recipes of the polymer composite.

Sample	K/ Al ₂ O ₃ (g)	[NH ₄ PAA] (mL)	[AA] (Mass % to AA)	[MBA] (mass%) relative to [AA]	[KPS]/[MS] (mass%) relative to [AA]	[H ₂ O] ml
K -8AA	42 / -	17	8	1	0.5/0.5	35
K-10AA	42 / -	17	10	1	0.5/0.5	35
K-12 AA	42 / -	17	12	1	0.5/0.5	35
K-14AA	42 / -	17	14	1	0.5/0.5	35
Al - 15AA	- / 42	17	15	1	0.5/0.5	35
KAl-20AA	21 / 21	17	20	1	0.5/0.5	35
K5Al-20AA	9 / 33	17	20	1	0.5/0.5	35
K10Al-20AA	17 / 25	17	20	1	0.5/0.5	35
10KAl-20AA	25 / 17	17	20	1	0.5/0.5	35
5KAl-20AA	33 / 9	17	20	1	0.5/0.5	35

2.3. Characterization

The IR spectra of the samples were recorded on a Model 500, Nicolet FTIR instrument by averaging 32 scans with 4 cm⁻¹ resolution, using the KBr pellet technique.

TGA- DTG was performed on a TA Instruments SDT600 thermo gravimetric analyzer. The thermographs were obtained at a heating rate of 20°C/min, using 5–10 mg of sample. The experiments were performed under a 100 mL/min nitrogen flow.

Scanning Electron Microscopy (SEM) analyses were carried out on a XL30 Philips scanning electron microscope, at an acceleration voltage of 20 kV.

The porosity of the burned bodies (ε) was determined with the following equation:

$$\varepsilon = \frac{m_f - m_i}{m_i} \cdot 100 \quad (1)$$

Where: m_i is the initial mass of the sample and m_f –final mass of the sample after being kept 24 hours in distilled water at room temperature.

Sample density was determined by the Archimedes method using the:

$$\rho = \frac{mp_{air}}{mp_{air} - mp_{liq}} \cdot \rho_{liq} \quad (2)$$

Where:

- mp_{air} – the sample mass in air;
- mp_{liq} – the sample mass in liquid, calculated with Archimede formula;
- ρ_{liq} – density of liquid at room temperature.

The average diameter of the pores d_p and the number of pores per cm^2 , were determined by BET method and optical microscopy.

In order to assess the hydrodynamic behavior of ceramic foams an experimental plant was built, and it is presented in Fig. 2.

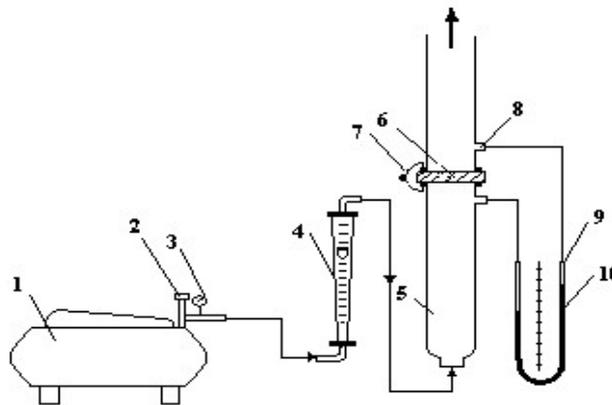


Fig. 2. Scheme of experimental plant for assessment of hydrodynamic behavior of ceramic foams.

The atmospheric air is fed using compressor (1), with a flow controlled by valve (2) and measured with the flow meter (4) at a pressure assessed with the manometer (3) into the filter cartridge (5) having a porous plate (6). The last is mounted between the 2 sections of the filter cartridge (5), being sealed with the system (7). The filter cartridge (5) has 2 intakes on the 2 sites of the porous plate for measuring the pressure drop with the differential manometer (9) having a colored alcohol (10) as manometric liquid. The range of air flow was 3000- 7000 L/h, in order to have a turbulent flowing. The air characteristics at determination

temperature of 20°C were density $\rho=1.29 \text{ Kg/m}^3$ and viscosity $\eta= 1.8 \cdot 10^{-2} \text{ cP}$. Considering that the pores of filtering plate are parallel and with constant diameter, the pressure drop may be calculated with the Fanning equation:

$$\Delta p = \lambda \cdot \frac{h}{d_p} \cdot \frac{w_p^2}{2} \cdot \rho \quad (3)$$

In which:

- Δp – pressure drop in filter, N/m^2 ;
- λ – friction coefficient, dimensionless;
- h – thickness of the filtering ceramic foam plate, m;
- d_p – pore diameter, m;
- w_p – air rate into the pore, m/s;
- ρ – air density, kg/m^3 .

The air rate into the pore may be calculated with the following equation:

$$w_p = \frac{4 \cdot G_v}{\pi \cdot d_p^2 \cdot N_p} \quad (4)$$

In which:

- G_v – air volumetric flow, m^3/s ;
- N_p – number of pores of filtering plate. It can be calculated with:

$$N_p = n_p \cdot A_c = n_p \cdot \frac{\pi \cdot d_c^2}{4} \quad (5)$$

In which:

- n_p – number of pores per cm^2 of the ceramic foam;
- A_c – area of ceramic foam plate, cm^2 .

3. Results and discussion

3.1. Green body characterization

The obtained green bodies were characterized mainly by FTIR, TGA- DTG and SEM. In Fig. 3 are presented the FTIR spectra of green bodies obtained with kaolin (K) or alumina (Al). In all FTIR spectra the peaks of the polymer appear, namely the band at 1720 cm^{-1} , characteristic to C=O and the band at 1690 cm^{-1} , characteristic to COOH. The characteristic bands for CH and CH_2 at around 2900 cm^{-1} are hidden by the OH band, mainly of the water from inorganic part. Also, the characteristic bands of each inorganic compound are present, differentiating the composites.

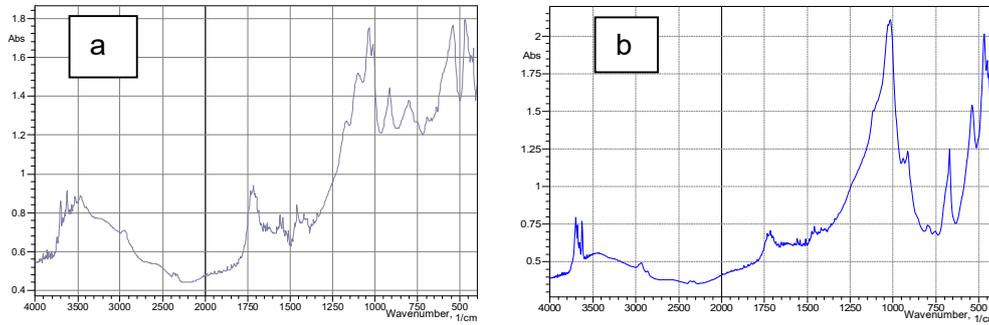


Fig. 3. FTIR Spectra of samples: (a)– K-15 AA, (b) – Al-15 AA.

Composites with mixtures of K and Al were characterized by TGA- DTG. In Fig. 4 and Fig. 5 there are presented the TGA and DTG curves for these green bodies. The TGA curves in Fig. 4, of synthesized composites show mass losses of 12-28%.

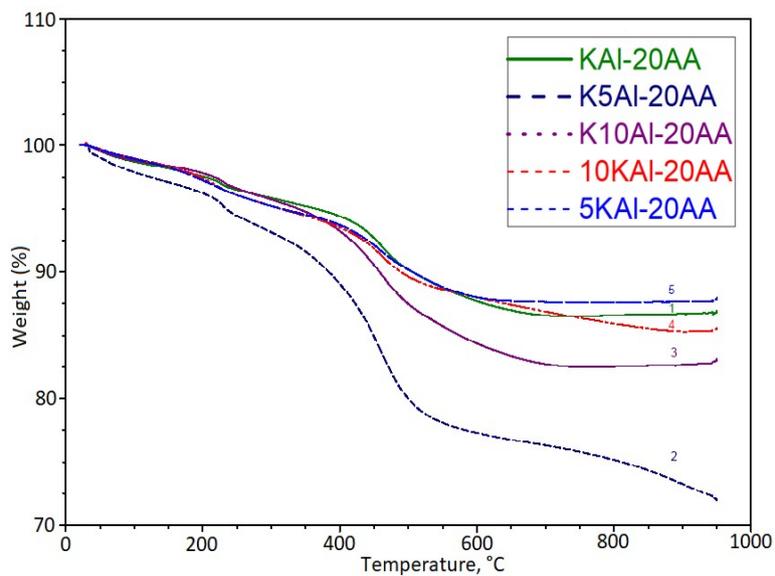


Fig. 4. TGA curves for samples in Table 1.

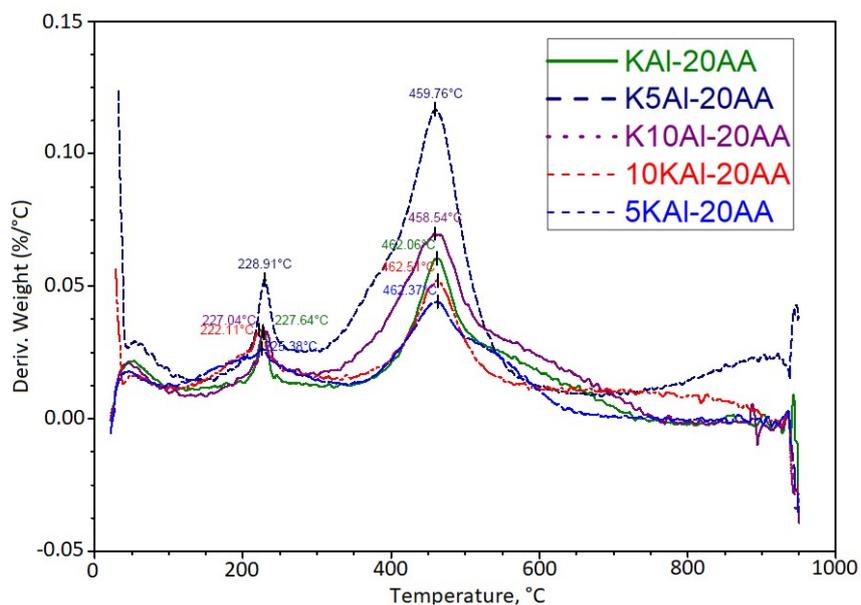


Fig. 5. DTG curves for samples in Table 1.

DTG curves in Fig. 5 show 2 maximal decomposition rates: that around 225°C is related with the polymer decomposition by decarboxylation while that around 460°C is due to the dihydroxylation of kaolin [13].

In order to understand the structure of composite hydrogel and of ceramic foams in Fig. 6 SEM images are presented for a green body K -15AA (a) and for the ceramic foam obtained from it (b). Very similar images were recorded for the other composites.

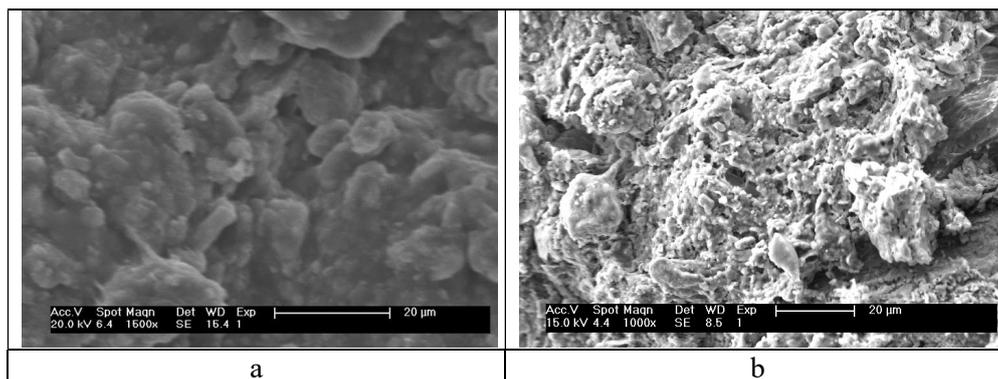


Fig. 6. SEM images of green dried body K -15AA and of the ceramic foams obtained from it (after the burning of the polymer and sintering of ceramic oxides).

3.2. Ceramic foams characterization

Ceramic foams obtained from kaolin at various AA concentration (8-16 mass%) in aqueous solution and those obtained from the samples in Table 1 were characterized by density, porosity, pore diameter and number of pores per cm². The results are presented in Table 2.

Table 2. Characterization of ceramic foams

Code of ceramic foam	Dimensions		Density	Porosity	Average pore diameter	Number of pores
	Average diameter	Depth				
	d	h				
	cm	cm	ρ	ϵ	d_p	n_p
	cm	cm	g/cm ³	-	mm	cm ⁻²
K -8AA	4.25	0.40	1.65	0.205	0.20	1632
K -10AA	4.35	0.60	1.03	0.223	0.15	2104
K-12 AA	5.15	0.52	1.67	0.247	0.15	2690
K-14AA	4.10	0.50	1.43	0.273	0.13	4116
K-15AA	4.00	0.50	1.51	0.260	0.13	3920
KAl-20AA	5.00	0.50	0.825	0.640	1.00	200
K5Al-20AA	4.50	0.50	0.873	0.620	0.80	180
K10Al-20AA	4.50	0.50	0.763	0.700	0.90	180
10KAl-20AA	5.00	0.40	0.767	0.640	1.10	250
5KAl-20AA	4.50	0.50	0.878	0.650	0.90	270

From Table 2 one can see that the ceramic foams had diameters between 4.00 and 5.15 cm and thickness between 0.40 and 0.60 cm. The samples prepared from mixture of K and Al, presented much lower densities than those prepared only from K (practically 2 times lower). A very significant increase in porosity was observed for the foams from K and Al mixtures (2-3 times higher), with much higher diameters of pores (5-10 times bigger), but with much lower number of pores per cm² (10-20 times lower) in comparison to the foams obtained only from kaolinite. The explanation for these features is the rather different compatibilities between inorganic compounds and the hydrogel matrix, as well as the different dimensions and shapes of K and Al powder particles.

3.3. Hydrodynamic behavior of ceramic foams

For calculating the friction coefficient, λ , considering its variation with the volumetric flow of air and the porosity of the filtering foam it was proposed a dimensionless equation:

$$\lambda = c \cdot \epsilon^m \cdot \text{Re}_f^n \quad (6)$$

In which Re_f is Reynolds fictive number calculated for the cross section of air flowing before passing the filtering plate and being calculated with equations (7) and (8):

$$Re_f = \frac{w_f \cdot d_c \cdot \rho}{\eta} \quad (7)$$

$$w_f = \frac{4 \cdot G_v}{\pi \cdot d_c^2} \quad (8)$$

In which:

- w_f – fictive rate of air, m/s;
- d_c –cartridge diameter, m.

By processing the experimental results for the first 5 samples in Table 2: K-8AA....K-14AA, the following equation was obtained, with an average error of 0.2%:

$$\lambda = 9.089 \cdot 10^4 \cdot \varepsilon^{2.024} \cdot Re_f^{-1.003} \quad (9)$$

In Fig. 7 it is shown the variation of the friction coefficient for the kaolin ceramic foams depending on the volumetric air flow. It is observed a nonlinear decrease of λ with the increase in air flow. It seems that the increased AA concentration at the preparation of green bodies, leads to an increase in friction coefficient, because as shown in Table 3 the pore diameter is lower.

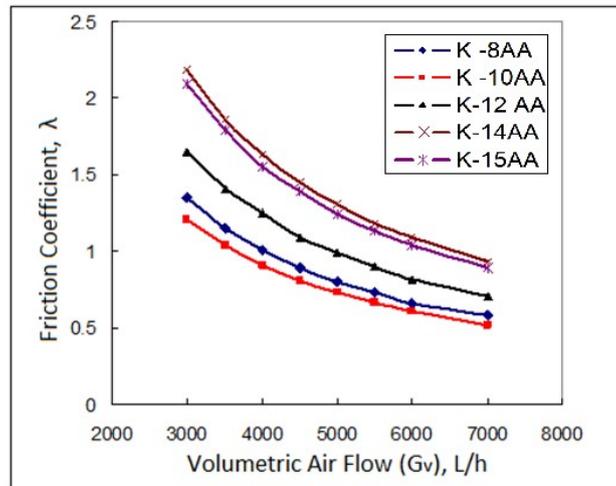


Fig. 7. The variation of the friction coefficient with the air volumetric flow for the samples prepared using only with K, at different AA concentration.

The Fig. 8 presents the influence of the porosity of the ceramic foams on the friction coefficient at 3 air volumetric flow for the same samples, obtained only with K. It seems that the increase in air volumetric flow, leads to a reduction in the friction coefficient. Independently on the volumetric flow, it is an optimal porosity of the filtering material of around 0.22, at which the lower friction coefficient occurs.

For the ceramic foams obtained using mixtures of K and Al, the following empirical equation was determined with an error of 1.16%:

$$\lambda = 2.331 \cdot 10^4 \cdot \varepsilon^{-0.523} \cdot \text{Re}_f^{-0.978} \quad (10)$$

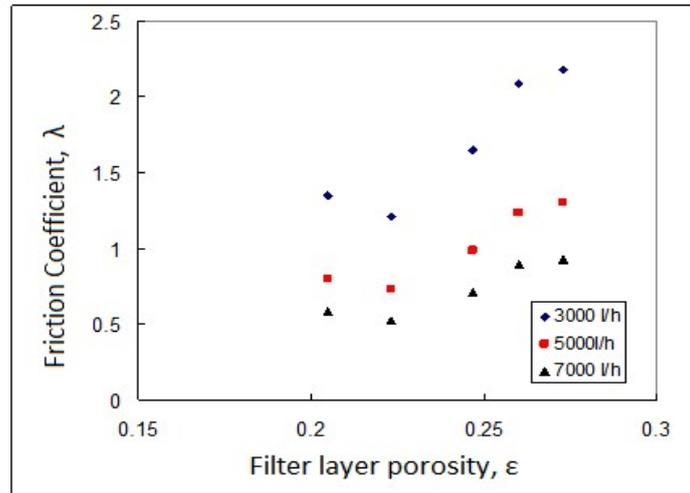


Fig. 8. The variation of the friction coefficient with the porosity of the filtering ceramic foam.

Also, in the case of ceramic foams prepared using K and Al mixtures the curves in Fig. 9 show a nonlinear decrease in friction coefficient with the increase in air volumetric flow. The friction coefficients are much greater than in the case of kaolinite ceramic foams.

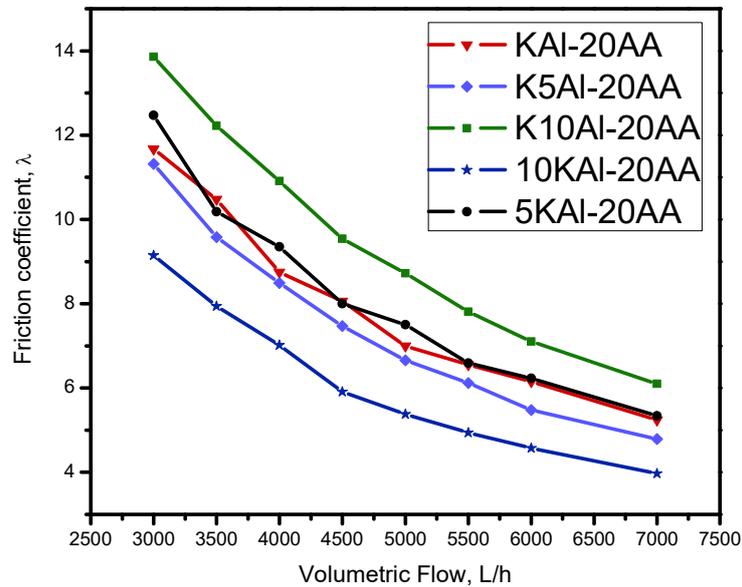


Fig. 9. The variation of the friction coefficient with the air volumetric flow for the samples prepared using mixtures of K with Al.

4. Conclusions

The gel casting method using AA- MBA hydrogel and inorganic compounds such as K and Al, allow the obtaining of ceramic foams for gases filtering. FTIR spectra proved the existence of polymer hydrogel and inorganic compounds in green bodies. TGA- DTG results proved that the hydrogel decomposes at around 225°C. The mass loses of dried green bodies was 12-28 % in the studied temperature range, showing the necessity of greater temperature for complete polymer burning. The assessment of density, porosity, average pore diameter and number of pores per cm² revealed a significant difference between foams prepared only from K and those prepared from mixtures of K with Al. The experimental plant allowed determining the model equations for friction coefficient. The measurements proved that between the 2 kinds of ceramic foams it is also a noteworthy difference in terms of hydrodynamic behavior. The best hydrodynamic characteristics was recorded for the foam prepared from K without Al.

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