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Application of the Ergun´s equation in porous ceramic based on CaO-stabilized ZrO_2

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Abstract

The study of the permeability in porous ceramics with potential application as filters is essential because this parameter includes a number of processing variables such as porosity and pore size of great importance in the development of porous media. The knowledge of the relationship between permeability and these variables, provide a better criterion to determine the process variables that result in an optimization of the permeability. The optimization of this parameter is a basic requirement for an adequate operation of the ceramic as a filter material. In this study, the permeability of porous ceramic prepared from different compositions of the mixture of ZrO_2 and a high alumina cement with 30 wt% CaO and sintered at 1400 ° C was experimental and theoretically evaluated. Theoretical evaluation of permeablity was performed using the Ergun´s equation, which describes the permeability constant as a funtion of the porosity and mean pore size of the porous material

Keywords: porous ceramic, permeability, Ergun.

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1. Introduction

In the field of filtration/ separation processes, dust gas pollutants and removal of contaminants, the gas permeability of porous ceramics is extensively studied [Adler, J. 2005]. For these industrial applications of the porous ceramics is necessary to know the relationship between pressure loss and permeability and, thus the optimization of permeability during filtration will reduce the costs of the filtration process.

Permeability indicates the material's ability to allow the passage of a fluid and is a specific property of the porous medium .

A theoretical estimation of permeability constant k_1 from porous structure parameters can be made by following the well known Ergun's equation [Bird et. col., 1973]. The permeability is described as a function of the mean particle size and porosity for porous granular media formed by a non consolidated packed bed of spherical particles of identical size , in a laminar flow conditions. Thus, k_1 is given by

$$k_1 = \frac{\varepsilon^3 d_p^2}{150(1-\varepsilon)^2} \qquad (1)$$

where ε is the porosity (pore volume fraction), d_p is the equivalent diameter of particle of the porous media [m].

The particle diameter can be estimated from the definition of hydraulic radius for spherical particles making the porous media:

$$d_p = 1,5\frac{(1-\varepsilon)}{\varepsilon} d_c \qquad (2)$$

where d_c [m] is the average pore diameter of the structure.

Combining equations *(1)* and *(2),* the evaluation of k_1 can be made considering that porous structure can be represented by two parameters such as the pore volume and the mean pore size or certain characteristic length. However, Eq *(1)* is deduced considering numerous assumptions including that the flow regime is laminar and that the porous medium is granular, unconsolidated and consists of spherical particles, and thus some discrepancies between predicted and measured values arise. Therefore, the experimental evaluation of permeability is essential for an optimization of the microstructure of the porous ceramic through processing.

In this study, a comparison between the measured permeability of porous ceramics and the predicted value using Ergun´s equation is given. The porous ceramic was prepared by powder processing of a mixture of monoclinic zirconia (m-ZrO_2) and commercial calcium aluminate cement . The experimental permeability of the ceramic was evaluated by the N_2 permeation at room temperature. The structural parameters such as pore volume and pore size was determined from the pore size distribution measured by Hg intrusion porosimetry . The influence of the chemical composition on the permeability and its relationship with textural characteristics of porous ceramic are examined.

2. Experimental

2.1. Materials and Preparation of ceramic disks

Porous ceramics were prepared by powder processing from a commercial mixture of m-ZrO_2 and high alumina cement (Secar 71) which approximately consists of 70 wt% of Al_2O_3 and 30 wt % CaO, are used in this work . Powder mixtures of ZrO_2 containing 5, 30 and 50 mole% CaO in ZrO_2 were formed by uniaxial pressing technique in a shape of discs of 30 mm in diameter and 5 mm thick and subsequently sintered at 1400 ° C- 2h in a furnace at a heating /cooling rate of 5 ºC/min.

The pore size distribution, volume and mean pore radius of the ceramic were determined by mercury intrusion porosimetry. The measurements were carried out in the porosimeter Carlo Erba 2000, Italy. The open porosity is calculated from the maximum intrude Hg volume.

2.3. Permeability

The experimental permeability of ceramic disks produced from the various compositions and sintered at 1400 ºC was carried out by N_2 permeation at room temperature. The method consists by passing the gas through the porous ceramic in an apparatus described elsewhere [Bruni, et al 2010]. The pressure drop across the ceramic was measured as a function of gas flow through it, being the sectional cross area and the thickness of the specimen in the flow direction known quantities.
The experimental curves of pressure drop and volume flow were analyzed according to Forchheimer's equation and Darcy law (Eq. 3 and 4, respectively) considering in both laminar flow of a compressible gas through a granular porous ceramic [Innocentini et col. 1999a, 1999b; Moreira , et al 2004].

Below are the expressions that describe these two models:

$$\frac{P_1^2 - P_2^2}{2P_2L} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^{\,2} \tag{3}$$

$$\frac{P_1^2 - P_2^2}{2P_2L} = \frac{\mu}{k_1} v_s \tag{4}$$

where the pressure drop for compressible gas (Pa) is given as $(P_1^2 - P_2^2)/2\,P_2$, P_1 and P_2 are the absolute values pressure measured at the entrance and exit of the porous medium [Pa], respectively; v_s is the gas velocity (m.s-1) calculated as the ratio between volume flow [m^3/s] and the cross section area [m^2] through the flow, μ the gas viscosity (Pa.s), k_1 the permeability (m^2), L the thickness (m), k_2 the inertial permeability (m) and ρ is the gas density (kg .m^{-3}).

The drop pressure vs. flow velocity data, measured as above described, were fitted to equations of both models and therefore the permeability constants k_1 and k_2 were evaluated. It is noted that these constants only depend on the structural characteristics of the porous medium.

The Forchheimer's number F_0 that considers the relationship between viscous and inertial forces (kinetics) and thus the error due to neglecting the non linear effects were evaluated with the following expressions:

$$F_0 = \frac{\rho v_s}{\mu}\left(\frac{k_1}{k_2}\right) \tag{5}$$

$$Deviation(\%) = 100\frac{F_0}{1+F_0} \tag{6}$$

2.4. Estimation / prediction of permeability using the Ergun´s equation.

The predicted permeability constant was obtained using Ergun's law (from equation 1). For each ceramic, a comparative study between the predicted and the measured permeability value is present.

3. Results

3.1 Experimental evaluation of the permeability and its variation with the ceramic compositions

Experimental pressure drop vs. velocity data (points) and fitted curves are shown in Figure 1.

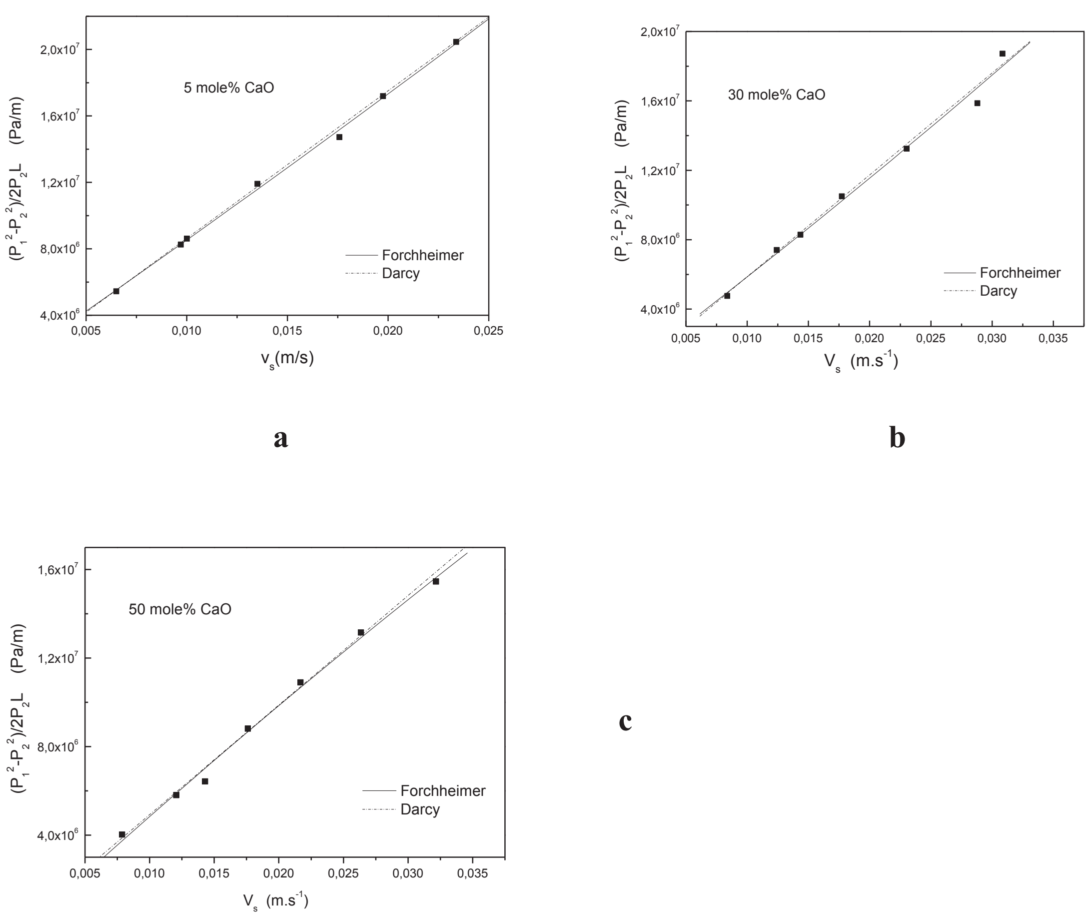


Figure 1: Experimental data and fitted lines corresponding to representation of Darcy´s and Forchheimer´s law of ceramic sintered at 1400 ° C for different CaO addition .

Figure 1 shows that a negligible deviation existed between experimental data and that of the lines presented in the range of velocity studied indicating that both equations of Darcy and Forchheimer´s are suitable to describe the experimental results.

Table 1 shows the resultant constants k_1 and k_2 determined by fitting the experimental data and the deviation parameter between both models, for each composite.

The basic difference between these two models is given by the dependence of the fluid pressure drop on the flow rate. Darcy's law which is derived from experiments conducted at very low flow velocities, considers that the pressure drop term of Eq 1 only represents the viscous effects. Thus, it provides a linear dependence between the pressure gradient and the velocity of fluid through the porous medium. On the other hand, the Forchheimer´s equation considers that the pressure gradient has a parabolic dependence on the flow velocity due to inertial and turbulence contributions [Innocentini et col. 1999b]. According to the low percentage of deviation shown in Table 1, in all cases is indistinct the application of one or another model to determine the permeability constant, as was clearly observed in Fig 1. Since the two models fitted well the experimental data, it is difficult to select the model that best represents the experimental permeability of the system.

Table 1: Experimental permeability *k1* and *k2* of ceramics evaluated from Forchheimer and Darcy´s models.

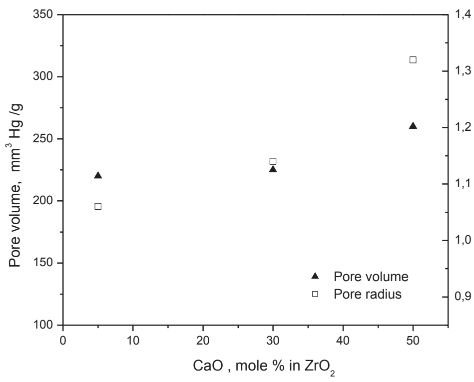
	Darcy	Forchheimer				
CaO in ZrO_2 Mole %	k_1(m^2)	k_1(m^2)	k_2(m)	k_1/k_2	F_0	Deviation (%)
5	2.20E-14	2.14E-14	7.18E-10	2.98E-05	0.027	2.67
30	3.06E-14	3.34E-14	9.28E-10	3.60E-05	0.045	4.27
50	3.63E-14	3.31E-14	9.8E-10	3.38E-05	0.041	3.92

Table 1 shows that it is valid to apply Darcy's law to evaluate the experimental permeability constant. Therefore, the Darcian permeability k_1 can be considered as the representative permeability of the ceramics studied. According to Eq. 4, the permeability (k_1) is inversely proportional to the slope of each fitted line and thus Figure 1 also shows that the permeability of the ceramic increased with increasing the CaO addition.

3.2 Application of Ergun´s Equation for predicting the theoretical permeability

The permeability constant k_1 was predicted by Ergun's equation (1) using the textural parameters obtained by Hg porosimetry.

The pore size distribution and mean pore radius of the ceramic discs sintered at various temperatures were determined by Hg intrusion porosimetry. Figures 2 a and b show the effect of the various contents of CaO in the starting composition on pore volume , mean pore radius and the witdh of the size distribution. The samples had a monomodal pore size distribution which was composed by pores having the most frequent pore radius near to 1 μm. High CaO concentration shifted the most frequent pore radius to higher values from 1.1 to 1.3 μm. Also the maximum intruded volume of Hg increased with increasing CaO. In particular, the composite containing 50% mol CaO exhibited a wider pore size distribution in which the coarser fraction with pore radius above 1.5 μm notably increased.



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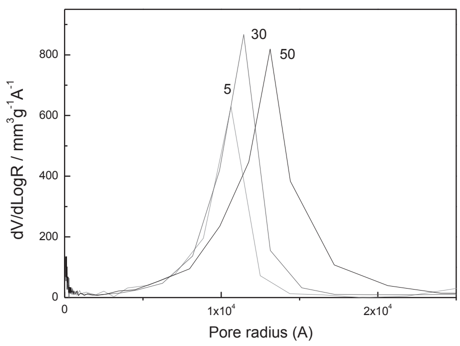

b

Figure 2: a) Pore volume and pore size vs. CaO content and b) pore size distribution for the ceramics with 15, 30 and 50 mole %CaO in ZrO_2 sintered at 1400 ° C.

Table 2: Experimental and theoretical values of permeability of ceramic sintered at 1400ºC and its deviation.

CaO in ZrO_2 Mole %	Darcy $k_1\,(m^2)$	Ergun $k_1\,(m^2)$	Pore radius (μm)	Deviation **(%)**
5	2,20E-14	3,17E-14	1.06	44
30	3,06E-14	3,82E-14	1,14	25
50	3,63E-14	4,07E-14	1,32	13

Table 2 shows that the theoretical k_1 exceeded the value obtained experimentally. Nevertheless, the predicted permeability followed the same behavior in relation to morphology and composition of the ceramic . Thus high k_1 resulted with increasing pore size and content of CaO.

The deviation between experimental and theoretical permeability may be associated to the numerous assumptions used to derive the Ergun equation. The model is based on the hydraulic radius which is not appropriate as a parameter for describing the characteristic length of the porous medium due to its complex porous structure. The particles forming the porous granular media have different shapes and sizes and they are not spherical nor of uniform size as assumed by Ergun. The actual porous medium consists in a randomly packed conduits with irregular shape and size, sensitive to change as the densification of the porous microstructure occurred by sintering at 1400 ºC , and not as a set of parallel conduits of cylindrical geometry as assumed in the model of Ergun. Consequently , the actual length the fluid path is higher than that predicted by the model. Moreover, the particles of granular media differ in morphology and size, having as result a greater flow resistance. For this reason experimental permeability was slightly lower than the theoretical value. This result agrees with previous studies showing that high densification of the ceramic leads to lower volume of open porosity.

The use of more complex models for predicting the permeability attributes this result to the increase in tortuosity of the porous medium.

The porous structure becomes more complex as densification ceramic occurs and therefore, can not be represented by the pore volume and mean pore radius. The use of these parameters is a simplification that does not consider the variation of other important microstructural characteristics of porous ceramic media (geometry and interconnection between pores, different width of the pore size distribution, etc.) produced from the different compositions during the sintering at 1400 ° C.

On the other hand, previous studies reported that Hg intrusion porosimetry which is an easy and widely used technique to determine the pore size distribution of mesoporous materials, has certain problems of data interpretation with different pore types [Kaufmannw, J. 2009].

4. Conclusions

N_2 permeability of porous ceramics based on ZrO_2 and calcium aluminous cement was evaluated by fitting the measured pressure drop vs. flow velocity curves with the Darcy and Forchheimer´s equations. Since the contribution of the viscous forces to the pressure gradient was greater than the inertial forces, Darcian permeability k_1 was found representative of the gas transport flow through the porous ceramic composites. Applying Ergun´s equation resulted the estimated permeability k_1 greater than the experimental. Since the proximity between values was satisfactory (in the order of magnitude), this model was useful for the prediction.

Darcian permeability k_1 varied between 2-4x10^{-14} m^2 with increasing CaO content and resulted proportional to the increase in both the pore volume and the mean pore radius of the ceramic.

Ergun's equation led to higher values of the N_2 permeability constant with respect to that obtained experimentally. This deviation was attributed to the actual length path of the gas that is greater than the idealized length defined by that model.

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