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Permeability of porous ceramic based on calcium carbonate as pore generating agent

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Abstract

This study concerns the processing and characterization of porous ceramics based on low cost mineral raw materials for environmental applications. Three formulations were tested with calcium carbonate as pore generating agent and different proportions of kaolin, potassic feldspar, albite, quartz and white clay. Ceramic bodies were formed by pressing, heat treated up to 1180 °C and characterized for porosity, flexural strength, air permeability and microstructural aspects. The resulting bodies displayed apparent porosity (28–32%), flexural strength (7–29 MPa), permeability coefficients ($k_1 \cong 10^{-15}$ m^2 and $k_2 \cong 10^{-11}$ m) and average pore size (0.706–1.137 μm) suitable for membrane separations. The formulation containing 50% kaolin, 20% limestone, 10% potassic feldspar, 10% albite and 10% quartz (dry basis) was considered the most suitable for separation of suspended solids from liquid suspensions (microfiltration).

Keywords: A. Processing; B. Porosity; Ceramics; Permeability; Microstructure

1. Introduction

Removal of soluble and suspended contaminants from liquid or gaseous streams is a vital concern in all industrial processes that must comply with stringent environmental regulations. Filtration and adsorption are two physical operations that, if properly designed, not only allows efficient stream purification but also economic recovery of concentrated contaminants [1–7].

Despite some divergences in terminology, filters for air pollution control and membranes for water or wastewater treatment are both pressure-driven semi-permeable barriers that remove contaminants according to their size from the carrier fluid by a combination of mechanisms [8]. Ideally, the separation should occur only on the external surface of the filtering medium in order to prevent progressive and irreversible clogging of the structure with contaminants and thus make their recovery easier by cleaning. It is also desirable that the filtering medium do not operate under excessive fluid pressure drop to minimize pumping costs and the risk of failure. However, collection efficiency, permeability and mechanical strength are differently affected by the features of the medium, such as the amount, shape, size and interconnectivity of pores. In general, enhancement of permeability can be achieved by increase in the amount and/or size of pores, but then the filtering barrier becomes less efficient and more prone to damage. On the other hand, suitable removal of nanosized aerosol particles or soluble compounds can only be achieved on the filter surface if pores are accordingly dimensioned in the nanoscale range, which may raise the flow resistance to non-economic levels and again expose the medium to failure [9–12].

Porous ceramics have become key materials in demanding filtration applications because their microstructure and composition can be tailored to present a very favorable combination of features, including high permeability, specific surface area,

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List of symbols

A	cross-sectional area normal to the flow
d_{pore}	average fluid dynamic pore diameters
k_1	Darcian permeability coefficient, in reference to Darcy's law
k_2	non-Darcian permeability coefficient, in reference to Darcy's law
L	sample thickness
P_i	absolute air pressure at the entrance of the sample
P_o	absolute air pressure at the exit of the sample
Q	volumetric flow rate
v_s	superficial velocity of the fluid
$\Delta L/L_o$, LS	linear shrinkage
ε	porosity
ε_a	apparent porosity
μ	viscosity of the permeating fluid
ρ	density of the permeating fluid
ρ_a	apparent density

mechanical strength, thermal inertness and chemical resistance to aggressive environments [13,14]. Indeed, when based on cheap raw-materials, simple processing routes and optimized surface-to-volume shapes, porous ceramics can be very competitive to adsorptive and filtering polymeric materials in many industrial and environmental applications.

The choice of a given fabrication route [13–15] depends ultimately on the resulting microstructure, properties and shape desired for the final product and on application considered [16,17]. On the other hand, the correct choice of sacrificial fillers and gas-generating phases, including graphite, hydrates and carbonates, can generate ceramic bodies with pores in a suitable range required for separation of very small contaminants [11,18].

In order to minimize the fluid flow resistance and also cope with the great volumes of aerosol and wastewater streams that must be treated, ceramic media are usually operated in modules, which allow the largest possible filtration area packed into the smallest possible equipment volume [3,8]. From an economic point of view, it is therefore desirable that the filtering media be produced in shapes with the highest surface-to-volume ratio and with the cheapest raw materials. The preferred shapes for ceramic filter media in large-scale applications are flat sheets and tube bundles, while in laboratory duties discs in a range of standard diameters are available [8].

Noble raw materials for processing of ceramic filters and membranes include alumina, zirconia, titania and silica [3,8]. However, such materials are too expensive and for this reason mineral-based ceramic substitutes have been recently considered due to their low costs and additional functions [19–25]. Clays, silicon carbide and fly ash are examples of abundant and low cost materials which need lower firing temperature in comparison to metal oxide materials.

In this work, different formulations based on low cost raw materials available in Brazil and with limestone as pore generating material were evaluated for producing porous ceramics to be used in environmental applications. Kaolin, feldspars and white clay are not just available and cheap raw materials, but typical on the obtainment of porcelain-based ceramic compositions, i.e. compositions presenting relatively high bending strength and compressive strength [26]. The thermal, physical and fluid dynamic properties of sintered bodies were experimentally assessed and correlated with the desirable features of filtering media for gas cleaning and membrane separation.

2. Experimental procedure

Three formulations (Table 1) based on previous works [23,27] were prepared containing kaolin, limestone (as source of calcium carbonate), potassic feldspar, albite, quartz, and white clay (Colorminas Colorifício e Mineração, Brazil).

All powders presented particle sizes inferior to 45 μm (325 mesh sieve). Formulations were selected due to their low cost and appropriated thermal and mechanical resistances to applications at temperatures up to 1000 °C. Potassic feldspar ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$) were flux agents, i.e. carrier raw materials of alkali elements to reduce sintering temperature. White clay and kaolin were used to allow the formulation to be molded; kaolin was also important to balance the chemical composition of the ceramic formulation. Quartz was used as structural element and limestone (calcium carbonate) as pore generating agent.

Formulations were wet ground into a jar mill with solids content of 67 wt% and 33 wt% of water for 5 h. The suspensions were passed through a 200 mesh sieve (75 μm), dried at 80 °C for 24 h and then disaggregated (35 mesh sieve, 425 μm) to obtain the powder mix to form the compact samples by pressing. Thermal behavior of the formulations was evaluated by thermogravimetric analysis (TGA Q500, TA Instruments, USA; 10 °C/min in air). From the thermograms, degassing temperatures of the samples were defined. Sintering temperatures were obtained by observing the shrinkage behavior ($\Delta L/L_o$, LS) in relation to temperature in an optical dilatometer (Misura® HSM ODHT 1400, Expert System Solutions, Italy; 5 °C/min in air). Powders (7 wt% water) of each formulation were pressed at 25 MPa in a uniaxial hydraulic press as bars with dimensions of 40 mm × 100 mm × 3 mm for mechanical tests and as disks with 40 mm of diameter and ~6 mm thick for permeability evaluation. After pressing, specimens were

Table 1
Formulations used in this study (wt% dry basis).

Formulation	Kaolin	Limestone	Potassic feldspar	Albite	Quartz	White clay
F1	25	10	10	10	10	35
F2	50	20	10	10	10	0
F3	50	20	13	13	4	0