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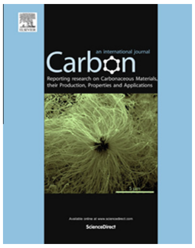

Tortuosity studies of cellular vitreous carbon foams

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ABSTRACT

The tortuosity of cellular vitreous carbon (CVC) foams having different bulk densities and different pore sizes has been investigated by a diffusion technique. The corresponding values were compared to tortuosities determined by two other different methods: acoustic on one hand, and tomographic on the other hand. Whereas acoustic tortuosities were slightly higher than diffusional ones but followed the same linear increase with CVC density, geometrical ones were much lower and presented the opposite trend. Such apparent discrepancies were discussed and justified, and the concept of constrictivity was used for that purpose. As diffusional tortuosity is the relevant parameter for accounting for transport phenomena, the permeability of CVC foams could be calculated from such tortuosity values, based on a realistic pore model of cellular carbon foams. The agreement between calculated and measured permeabilities was quite satisfactory.

1. Introduction

The term "tortuosity" has been used for a long time in petrophysics and in many other fields of science, but still it has no universal definition. The tortuosity is a way of describing the complexity of the structure of a porous material, i.e., how sinuous and interconnected it is. According to such definition, all tortuosity measurements should lead to similar values, but depending on the investigated property, on the type of measurement and on the model used to represent the structure of the material, the results can be somewhat different [1]. Tortuosity was formerly calculated from resistive or retarding effects occurring during transport phenomena, such as slowed down diffusion induced by a porous medium. From the oldest model of pore structure of Kozeny and Carman [1], the tortuosity τ is commonly defined as the ratio of an effective path length (throughout the porous medium) to the shortest path length (length of the porous medium), so that $\tau \geqslant 1$. Another parameter is also often used and should not be confused with tortuosity: the tortuosity factor τ^2 [1,2].

It is easy to understand that the effective path length can depend on the nature of the investigated transport phenomenon. For instance, liquid flow or electrical current inside the pores may use different pathways. However, tortuosity should ideally be related only to the structure of the material, and not to the nature of the considered transport phenomenon. Extreme care should therefore be taken to ensure that the experimental conditions are relevant to determinate the geometrical tortuosity. Anyway, whatever the definition of tortuosity and the way of measuring it, tortuosity studies of carbon materials are virtually absent from the literature.

In contrast, tortuosity has been much studied in geology for explaining fluid flow throughout stones and soils. Therefore, the first definition which has been developed is the hydraulic tortuosity in order to link the porous structure to the permeability. Kozeny, assuming that the pore space is a

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bundle of parallel but possibly tortuous, non-intersecting, tubes of identical radius and shape, defined the permeability k as [3]:

$$k = a\frac{L_0^2\varepsilon}{\tau^2} \tag{1}$$

In Eq. (1), a (dimensionless) is a constant which value depends on the pore model, ε (dimensionless) is the porosity and, according to theory of Kozeny and Carman, the characteristic length L_0 is such that:

$$L_0^2 = \frac{1}{2}\left(\frac{V_p}{S_p}\right)^2 \tag{2}$$

V_p and S_p being the volume and the surface of the open pore space, respectively. The theory of Johnson, Koplik and Schartz (JKS), or that of Katz and Thompson (KT) [4], can be used to get more precise values of the parameter L_0. Nevertheless, based on Eq. (1), the tortuosity can be determined through permeability studies. However, in such measurements, viscous effects can occur inside the porous media, taking place aside channel walls and locally retarding fluid flow. As a consequence, the calculated value of tortuosity can be easily overestimated.

As the aim of most reported studies was the determination of the permeability, the tortuosity had to be determined by an independent way. A widespread method consists in calculating the formation factor F, which is the inverse of the relative electrical conductivity σ_r of a porous medium saturated by an electrolyte, i.e., F is the ratio of the conductivity of the pure electrolyte (σ_0) to the effective conductivity of the medium (σ_{eff}). Taking Eq. (2) into account, the formation factor F (dimensionless) reads:

$$F = \frac{1}{\sigma_r} = \frac{\sigma_0}{\sigma_{eff}} = \frac{\tau^2}{\varepsilon} \tag{3}$$

However determining τ through the measurement of F supposes that the porous medium is an electric insulator which can be filled with a conductive liquid.

In order to determine the tortuosity in conductive media, such as carbon-based composites, the diffusion of ions [4] or more frequently of gases [2,5–13] have been frequently used. In both cases, the formation factor is the ratio the of diffusion factors in the bulk to those in the porous medium. The porous medium is thus used as membrane, and the amount of species diffusing across is measured as a function of time. Many studies based on such technique have been carried out. Most of them focused on stones or soils, much less on other kinds of porous materials [9,12,14–16]. So far, none has been dedicated to the determination of tortuosity of cellular vitreous carbon foams.

It has been shown that the determination of tortuosity by mass diffusion throughout porous media is only adequate for passive diffusion, i.e., without any reaction or convection to avoid coupling between different transport phenomena. The experimental description of such way of determining the tortuosity is explained in the next section. However, tortuosity can be measured by other different, more or less indirect ways, such as mercury porosimetry [17], nitrogen sorption hysteresis data [18], acoustic measurements [19–22] or tomography studies [23,24]. It was not the aim of this article to describe these methods but, as acoustics and tomography will be used for comparison with the diffusional tortuosity results reported here, a short description should be done.

In acoustics, the dynamical tortuosity $\alpha(\omega)$, where ω is the pulsation related to the frequency f according to $\omega = 2\pi f$, describes inertial and viscous effects occurring during the waves propagation in the fluid saturating the porous media [25]. As only one wave mode propagates (motionless skeleton), the porous material filled by air is called equivalent fluid. The dynamic density $\rho(\omega)$ of the equivalent fluid is defined as $\rho(\omega) = \rho_0\,\alpha(\omega)$, ρ_0 being the density of the fluid. Thus, the complexity of the medium and the viscous skins occurring along the cell walls increase the “effective” density of the fluid. When the frequency increases, the viscous skin depth decreases then the fluid, which can be considered perfect and incompressible, behaves according to the electric problem (Laplace equation). The geometrical tortuosity α_∞ is defined as the high-frequency limit of $\alpha(\omega)$. The determination of α_∞ is most of the times based either on the use of an impedance tube and of models linking the results with the porous structures (indirect or inverse methods) [19,25–28], or on direct ultrasound measurements [20,21,29,30].

Through X-ray microtomography, the investigated porous material can be modelled in three dimensions, and its properties can be analysed by some algorithms. The geometrical tortuosity is measured on 3D gray-tone images with methods based on geodesic reconstruction of the pores, or after a segmentation step by direct measurement of the shortest distance between two points in the pores. More details about these methods can be found elsewhere [23].

Considering the aforementioned, short, descriptions of the different ways of measuring tortuosity, different values can be expected for a same porous material. Indeed, for complex structures such as foams, different values of geometrical tortuosity can even be found, depending on the used mathematical definition. Moreover, most of the times, this determination does not take into account any pore constrictions (bottleneck effect) nor viscous effects which can occur in transport phenomena. For example, diffusional and electrical flows throughout a tube are proportional to the cross-sectional area of the tube. If there are some constrictions, the geometrical tortuosity should be lower than diffusional and electrical tortuosities. In hydraulic and acoustic phenomena, because of viscous effects occurring aside walls, the shortest path used by the fluid in the material may not correspond to the geometrical one.

Analysing a porous material’s behaviour in relation to its structure is a good start for optimising it for various potential applications. Many models of porous material indeed use the tortuosity parameter, therefore the latter should be accurately determined. The present work focuses on the characterisation of cellular vitreous carbon (CVC) foams derived from tannin-based rigid, organic, foams. Tannin-based CVC foams have already demonstrated their suitability for many applications such as thermal [31], acoustic [26] or electromagnetic [32] insulation. If their specific surface area is increased [33,34], the carbon foams can also be used as absorbents, porous electrodes or catalyst supports.

Different transport phenomena are involved in all these possible applications, and therefore different values of