Thermal Conductivity Models of Porous Materials

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Abstarct: The thermal conductivity theory for porous materials has been treated. Study of previous researchers has been discussed. The estimation of the thermal conductivity of porous material on a basis of a topological network obtained by image analysis techniques seems to be more accurate than the general model for conduction in a multiphase media proposed by Reynolds and Hough for the dielectric constants of mixtures and its thermal equivalent given by A. Simpson and Audry. Stuckes. The reason is that the Reynolds and Hough model supposed that the shape of the pores are spherical or disc shaped, while in the estimation of the thermal conductivity by image analysis, the method traits the real shape of the pores. Similar study done on the effects of bubbles on the hydraulic conductivity presented by Hunt and Manga, where they presented a model based on a single bubble dynamics to develop a model for a motion of fluid through a porous material.

Key words: Topological network, image analysis techniques, thermal conductivity, porous medium model

INTRODUCTION

The coefficient of thermal conductivity λ measured in W m.K⁻¹, is a physical property of substance, which characterizes its ability to conduct heat (Nashchokin, 1979). Solids may be classified according to their thermal conductivity into three kinds of materials, insolating material with a value of λ ranging from 0.02 W m. K⁻¹ for foamed polyurethane to 2 W m.K-1 for dense masonry materials. The best conductors of heat are metals with thermal conductivity varies from 3 to 458 W m.K⁻¹it may reach 2000 for diamond (Simpson and Audrey, 1986). The less heat conductors like most building materials have thermal conductivity from 3 to 5 W m.K⁻¹. Thermal conductivity of gases at atmospheric pressure varies from 0.006 to 0.18 W m.K⁻¹ isolating materials from 0.025 to 0.25 W m.K⁻¹ non metallic liquids 0.10 to 1 W m.K⁻¹ metallic liquids (Schmidt). 8.5 to 85 W m.K⁻¹ For the same materials there is a range of conductivity values, this variation is due to the moisture content, to the density, to the pressure, the impurities and, to the temperature variation (Leontiev, 1985). Thermal conductivity is greatly influenced by the moisture content of substance. Experimental studies have shown that the thermal conductivity increases substantially with an increase in moisture content (Simpson and Audrey, 1986). In addition the greater the volumetric density of a material, the fewer the pores in it and the greater is its thermal conductivity.

The thermal conductivities of heat insulating materials and building materials of a porous structure

increases linearly with rising temperature and lie in the range $0.02\text{--}3.0~\mathrm{W}~\mathrm{m}~\mathrm{K}^{-1}.$

Experimental studies have shown that for many materials the dependence of the thermal conductivity on temperature can be assumed to be linear.

$$(\partial \theta / \partial \tau) \lambda = \lambda_{\mathbf{n}} [\mathbf{1} + \mathbf{b}(\theta - \theta_{\mathbf{n}})] \tag{1}$$

where

 λ_0 = Thermal conductivity at the temperature θ_0 [K]

 $\theta = \text{Temperature } [K]$

b = Temperature coefficient determined by experiment

Heat transfer process in porous materials: The thermal conductivities of porous materials are greatly influenced by the gases filling the pores and have very small thermal conductivities compared with those of solid components. The increase in the thermal conductivity of porous materials with rising temperature is explained by the considerable increase in the intensity of radiation heat transfer between the surfaces of the solid of the pores through the air cells that separate them. The role of convection in the increase in the thermal conductivity becomes more important with the increase in the size of the air filled spaces in the material. For pores smaller in diameter than a few mm, gas convection cannot occur and the heat transfer through the gas depends only on collisions between the molecules within the pores, the gas conductivity is that of still gas. In highly porous materials

where the contribution from the solid is small, the thermal conductivity is typically in the range 0.02 to 0.04 W m K⁻¹. In a very good insulants such as foamed polyurethane, the gas conduction component is minimized by replacing air with large molecule gas such as trichloromonofluormethane. In air filled super insulants the conductivity lay be effectively reduced below that of still air by restricting collisions between gas molecules. This is achieved in manufacture by a prodomiance of pore sizes of the order of, or less than, the mean free path of the air molecules ($\leq 10^{-7}$ m). Although the radiative component may become significant at a very low densities at a high temperature, it is generally small compared with conduction (Simpson and Audrey, 1986). That is why the effective coefficient of heat conductivity of a porous material has a complex nature and is a fictitious quantity. It is equal to the thermal conductivity of some homogeneous body of the same shape and size through which the same amount of heat is transferred under the given boundary temperature conditions.

Theoretical analysis of thermal conductivity of porous material: It is well known that the porous material can be divided in two main classes a macro porous structure in the solid matrix and a macro porous cellular structure (the air bubbles). The macro pores may be filled with gas or liquid, or filled with both of them with different percentages and the thermal behaviour lies between that of its components and depends on the volume fraction of each and its distribution. To estimate the thermal conductivity from the properties of the individual components, It is necessary to choose a model which represents the distribution and shape of the component phases with the mixture. The models proposed fall into one of two categories a two continuous phase medium or a suspension in which one continuous phase forms a matrix in which all other phases are embedded as inclusion. These may be of arbitrary shape or specified geometry and their distribution may be random or ordered. For industrialized porous material such as Aerated Autoclave Concrete (AAC), the size of the air bubbles in the AAC allows direct observation by optical microscopy, image analysis is a particularly well adapted technique. Laurent and Frendo-Rosso have developed tools to characterize the cellular porous phase by using the image analysis method and they studied the relationship between structure and thermal conductivity of AAC.

Parallel and series arrangement models: For the parallel model the heat flow is parallel to each layer, a constant temperature gradient is applied to each phase and it can readily be shown that

$$\lambda = V_0 \lambda_0 + V_1 \lambda_1 \tag{2}$$

where λ is the thermal conductivity of the composite λ_0 is the solid thermal conductivity and V_1 is the volume fraction of the pores

 λ_1 is the conductivity of the gas filling the pores and V_0 = 1- V_1

By neglecting the conductivity of the gas filling the pores λ_1 Loab (1954) had obtained the following equation

$$\lambda = \lambda_0 (1 - V_1) \lambda \tag{3}$$

For the series model and when the heat is applied normally to the layers, the relationship becomes

$$\frac{1}{\lambda} = \frac{V_0}{\lambda_0} + \frac{V_1}{\lambda_1} \tag{4}$$

For all compositions of the two phase system, the series model has the lowest conductivity and the parallel model the highest. Since there is no general theory to represent the conductivity of all compositions of a two phase complex material, these simple models re particularly useful in determining the normal bounds of λ .

The general structure of real materials can be considered as combinations of the series and parallel arrangements. The form of these combination is unknown and various formulae for the conductivities between the limiting cases have been proposed either empirically or formulated on the basis of a simple model. These can be generalized in the form.

$$\lambda^{n}\!=\!\sum V_{r}\lambda_{r}^{\ n} \tag{5}$$

where n is a constant and Vr is the volume fraction of the r^{th} phase. As n approaches zero λ^n equals $1+ n \log \lambda$ and

$$\log \lambda = \sum V_r \log \lambda_r \tag{6}$$

This is the so-called logarithmic mixture rule which on rearrangement gives the geometric mean

$$\lambda = \lambda_0 V^0 \lambda_1 V^1 \dots \lambda_r V^r \tag{7}$$

since $\sum V_r = 1$

DeVries (1952) attempted to evaluate the porous medium thermal conductivity when it is fully saturated of water λ_{sat} and to also evaluate the thermal conductivity of the solid grains λ_{s} using models based on the arithmetic and

harmonica means, assuming lamellar, fibrous and spherical grains, but it was noticed that all of them were unsatisfactory and that when they did not underestimate λ_{sat} and λ_{s} , the results were physically inconsistent.

A more recent formula for the geometric mean given by Nathan Mendes and co, where they considered a model base on the geometric mean of the medium components.

$$\lambda_{\text{dry}} = \lambda_{\text{S}}^{(1-\eta)} \lambda_{\text{air}}^{\eta} \tag{8}$$

$$\lambda_{sat} = \lambda_{S}^{(1-\eta)} \lambda_{H20}^{\eta} \tag{9}$$

or explicitly for

$$\lambda_{s} = \left(\frac{\lambda_{dry}}{\lambda_{air}^{\eta}}\right)^{\frac{1}{(1-\eta)}} \tag{10}$$

Rayleigh (1982) and Maxwell (1904) presented calculation for electrical permittivity of a continuous medium containing spherical phase. The corresponding thermal case is given by Eucken (1940).

$$\lambda = \frac{\lambda_0 V_0 + \frac{3\lambda_0 \lambda_1 V_1}{2\lambda_0 + \lambda_1}}{V_0 + \frac{3\lambda_0 V_0}{2\lambda_0 + \lambda_1}}$$
(11)

Another equation was given by Brailsford and Major (1964) where they considered a random 2 phase system in which two single phases in the correct proportions are each assumed to be embedded in a random mixture of the 2 phases, this mixture having conductivity equal to that calculated for the two phase assembly. They obtained:

$$\begin{split} \lambda &= 1/4[(3V_0-1)\lambda_0 + (3V_1-1)\lambda_1 + \\ &[(3V_0-1)\lambda_0 + (3V_1-1)\lambda_1]^2 + 8\lambda_0\lambda_1]^{1/2} \end{split} \tag{12}$$

the conductivity of 3 or more phases is given as

$$\lambda = \frac{\lambda_0 V_0 + 3\lambda_0 \lambda_1 V_1 / (2\lambda_0 + \lambda_1) + 3\lambda_0 \lambda_2 V_2 / (2\lambda_0 + \lambda_2)}{V_0 + 3\lambda_0 V_1 / (2\lambda_0 + \lambda_1) + 3\lambda_0 V_2 / (2\lambda_0 + \lambda_2)} \quad (13)$$

Bhattacharyya (1980) in connection with the thermal conductivity of fibrous materials has applied Fricke's approach to the electrical conductivity of a two phase medium, the model assumes that any single fibre can be treated as a spheroid whose major axis is very compared wit its minor axis.

$$\lambda = \frac{3\lambda_0 V_0 (\lambda_0 + \lambda_1) + V_1 \lambda_1 / (5\lambda_0 + \lambda_1)}{V_0 (\lambda_0 + \lambda_1) + V_1 / (5\lambda_0 + \lambda_1)} \tag{14}$$

where the fibres are represented by phase 1 in a continuous air phase 0.

Russel (1935) derived the effective thermal conductivity of dry porous material from the properties of its components gas and solid assuming a distribution of uniform cubic pores arranged in a simple cubic lattice

$$\lambda = \lambda_0 (1 - \alpha V_1) \tag{15}$$

where α is an empirical constant and V_1 is the porosity A generalized empirical equation

$$\lambda = \lambda_0 (1 - A) + A\lambda_1 \tag{16}$$

where

$$A = \frac{2^{n}}{2^{n} - 1} \left[1 - \frac{1}{1 + V_{1}^{n}}\right] \tag{17}$$

n>0 is an empirical exponent determined by the mode of packing, pore size, pore shape and emissivity inside the pore.

A general expression for thermal conductivity may be obtained by following the derivation of general equation for the dielectric constant of mixture given by Reynolds and Hough and analogy could be made for the heat flux and electric charge. In this analogy voltage is equivalent to temperature and heat flux to current density and temperature gradient to electric field.

The equation of heat flux U between two phases mixture averaged over the whole volume is given by

$$U = \frac{\int_{V_0}^{V_0} U dV + \int_{V}^{V_1} U dV}{V} = V_0 U_0 + V_1 U_1$$
 (18)

Where U_0 , U_1 are the average heat current densities in each of the phases.

Similarly the average temperature gradient T is given by

$$T = V_0 T_0 + V_1 T_1 \tag{19}$$

It is then assumed that the thermal conductivity of the mixture is given by

$$\lambda = \frac{U}{T} \tag{20}$$

And for each component

$$U_0 = \lambda_0 T_0 \quad \text{and} \quad U_1 = \lambda_1 T_1 \ U_1 \tag{21}$$

From Eq. 17-19

$$\lambda = \lambda_0 V_0 f_0 + \lambda_1 V_1 f_1 \tag{22}$$

$$1 = V_0 f_0 + V_1 f_1 1 \tag{23}$$

where

$$\mathbf{f}_0 = \frac{\mathbf{T}_0}{\mathbf{T}}$$
 and $\mathbf{f}_1 = \frac{\mathbf{T}_1}{\mathbf{T}}$

Rearranging Eq. 22 and 23 gives

$$\lambda = \lambda_0 + (\lambda_1 - \lambda_0) V_1 f_1 \tag{24}$$

this equation should be used when inclusion of phase one are dispersed in a continuous phase 0.

The same equation arranged but in another way

$$\lambda = \frac{\lambda_0 V_0 f_0 + \lambda_1 V_1 f_1}{V_0 f_0 + V_1 f_1}$$
 (25)

should be used when phases are roughly equal particle size. Figure 1 shows comparisons of models for thermal conduction in two phase media.

Laurent (1991) gives the thermal conductivity for a parallel model for the estimation of Autoclaved Aerated Concrete thermal conductivity by

$$\lambda = \frac{\left[\lambda_{sm}(1 - \epsilon_c) + \lambda_{sir}\epsilon_c\right]}{\tau} \tag{26}$$

where λ is the thermal conductivity of AAC

 λ_{sm} the thermal conductivity of the solid matrix

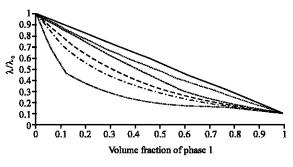
 λ_{air} air thermal conductivity

 ε_c rate of macroporosity measured by image analysis (explained in following paragraph)

τ tortuosity factor which is not measurable.

With the measured values of the thermal conductivity λ , it is possible to estimate this factor by:

$$\tau = \frac{\left[\lambda_{\text{am}} (1 - \varepsilon_c) + \lambda_{\text{air}} \varepsilon_c\right]}{\lambda} \tag{27}$$



Parallel model
Euken-maxwell mode phase 0 continious
Erailsford and major model
---- Geometric mean
Euken-maxwell model phase 1 continious
Series model

Fig. 1: Comparison of models for thermal conduction in two phase media

Tortuosity factor: Tortuosity is an important parameter that characterizes pore connectivity and fluid transport properties in porous media such as electrical conductivity, fluid flow, diffusion and velocity of sound (Johnson and Sen, 1988). Recent studies have shown that gas diffusion can be a powerful probe of porous media (Mair *et al.*, 1998, 2002).

The use of gas also allows to probe the time-dependent diffusion coefficient, D(t) over a wide range of length scales and to observe the long-time asymptotic limit which is proportional to the inverse tortuosity of the sample, as well as the diffusion distance (Johnson and Sen, 1988).

Determination of the thermal conductivity of porous materials by image analysis technique: The technique has been developed by Laurent and Frendo-Rosso for the study of the relationship between structure and thermal conductivity of AAC (aerated autoclaved concrete), the studied samples have been impregnated by an epoxy resin under vacuum conditions. Images are taken by means of black and white video CCD camera mounted on an optical microscope and then, they are transferred on a computer after digitalization by a frame-grabber card on a matrix of 512×512 image points or pixels. The rate of macroscopy is calculated just by counting the pixels of the porous phase and dividing the results by the size of the image. The pore sizes distribution is determined by using a method of successive apertures by discs of increasing radius. The mean advantage of this method is the possibility of making a porosimetry on a complex shape connected pores (Fig. 2).

A topological networks obtained by image analysis have been used to estimate the thermal conductivity of AAC. Two steps should be taken when building the

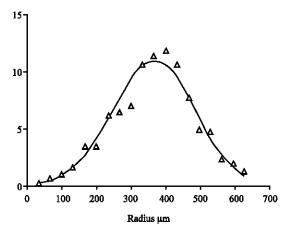


Fig. 2: Example of determination by image analysis of the pore sizes distribution

topological network, First a skeletton of the solid matrix is obtained by computing the median line graph of this phase. Then the missing paths going beneath or above the plane of the image are reconstructed applying criteria of minimum distance between unconnected branches (Thiel and Montavert, 1991).

Calculation of the thermal conductivity on the networks:

The skeleton of the solid matrix must be described as a graph, intersections between branches should be labelled and their coordinates measured. an electrical analogy can be applied using the formal similitude which exists between Ohm's law and Fourrier's law:

$$U = RI \Leftrightarrow \Delta T = \frac{L}{S\lambda_{sm}}Q$$
 (28)

Where U is the potential difference (V), R an electrical resistance(Ω), I the intensity (A), ΔT the temperature difference in (K), L length (m), Surface in (m²), λ_{sm} the thermal conductivity of the solid matrix (W m K⁻¹) and Q the heat flux (W).

If (x_i, y_i) and (x_j, y_j) are the coordinates of each link between nodes i and j, the admittance which correspond to the apparent thermal conductivity is noted by Y_{ij} , the thermal resistance by R_{ij} , the admittance must be calculated by:

$$Yij = \frac{\lambda_{sm} \times e}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}}$$
 (29)

Where e is the thickness of the link and could be estimated

$$e = \frac{N(1 - \epsilon_c)}{n_1} \tag{30}$$

Where N is the size of the image in pixels, ε_c the rate of macro porosity and n_1 the average number of links in a line

Laurent and Frendo Rosso, in their application of image analysis to the estimation of AAC thermal conductivity, they adopted the Y bus matrix representation that they build up by using the iterative algorithm proposed by Jegatheesan (1987). The algorithm consists in two basic operations, the first is to add a new node i connected to an existing one j by an admittance Y_{ij} , the second is to add a new admittance Y_{ij} between two existing nodes i and j. The apparent thermal conductivity is then given by:

$$\lambda = \frac{1}{\text{Ybus}} \lfloor N, N \rfloor \tag{31}$$

CONCLUSION

The thermal conductivity theory for porous materials has been treated. Studies of previous researchers has been discussed.

The estimation of the thermal conductivity of porous material on a basis of a topological network obtained by image analysis techniques seems to be more accurate than the general model for conduction in a multiphase media proposed by Reynolds and Hough for the dielectric constants of mixtures and its thermal equivalent given by Simpson and Audry. Stuckes. The reason is that the Reynolds and Hough model supposed that the shape of the pores are spherical or disc shaped, while in the estimation of the thermal conductivity by image analysis, the method traits the real shape of the pores. Similar work done on the effects of bubbles on the hydraulic conductivity presented by Hunt and Michael Manga (2003) where they presented a model based on a single bubble dynamics to develop a model for a motion of fluid through a porous material, they presented a complex pore geometry (Fig. 3a) as a network of cylindrical tubes (Fig. 3b). This geometric approximation is made in order to simplify the analysis. It also allows the use of well-established pore-scale results. While the geometry shown in Fig. 1b may not resemble typical porous.

The model proposed by Reynolds and Hough takes in account the shape and orientation of the inclusions or pores, as well as the thermal conductivities and volume fractions of the component phases. It has been shown that the most models proposed by other investigators can be derived from this general model. The inclusions in a matrix of randomly oriented disc shaped pores (or disc shaped low conductivity inclusions) or spherical pores

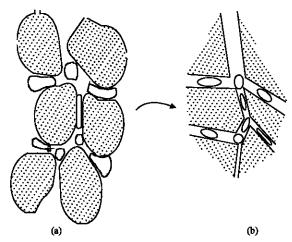


Fig. 3: (a) Schematic two-dimensional view of noncylindrical bubbles in non-cylindrical pore space (b) An idealized version of (3a) commensurate with cylindrical geometry, represented as a network of tubes

reduces the composite thermal conductivity. Thermal conductivity is substantially influenced by the nature of fluids filling the pores and their pressure, thermal radiation may be important when the pore size is significant.

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