Numerical Simulation of the Effect of Moisture on the Thermal Conductivity of Porous Ceramic Materials

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Abstract

A simulation model to analyze the influence of moisture content on the thermal conductivity of porous ceramic materials is developed based on the numerical integration of the energy equation. The experimental technique employed for thermal conductivity measurements is the hot wire parallel technique. The numerical model proposed is checked by evaluating the thermal conductivity of a hypothetical porous ceramic material containing different concentrations of water in its structure. The behaviour of the thermal conductivity as a function of temperature, as predicted by the model proposed in this work was experimentally verified by the authors for an unfired refractory concrete. © 1999 Elsevier Science Ltd. All rights reserved

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1 Introduction

A strong increase in the development and usage of ceramic materials has been noticed in the last decade. In several applications, conventional refractories may be replaced with some advantages, by monolithic refractories. Bakker[1] listed the advantages of these materials when compared with the previous ones:

(a) Quick installation and low construction costs.
(b) Possibility of fully anchored construction.
(c) Reduced and simplified furnace maintenance.
(d) Thermal conductivity one-half to one third that of fired brick, permiting thinner linings or improving thermal efficiency.
(e) Good thermal shock resistance.
(f) No joints (monolithic).
(g) Prefired shapes need not be stocked.
(h) Ready availability.
(i) Greater flexibility in design.

However, monolithic refractories have a mutant nature considering that their microstructure changes irreversibly during the initial heating as a consequence of the loss of adsorbed and crystalization water. So, drastic changes in the thermal conductivity are expected during the mutational period. The intensity of these changes is closely related to the moisture content, either as free water, or as water of hydration. The water inside a porous material absorbs part of the heat that propagates throughout the medium changing its temperature profile. Therefore, the thermal conductivity experimentally measured, is different from that which would be measured if no water was present.

An appropriate experimental technique to study the effect of moisture content on the thermal conductivity of that material is the hot wire technique.[2] It is an absolute, non-steady state and direct method, and therefore it makes the use of standards unnecessary. The first practical application of the hot wire technique was reported in 1949 by Van der Held and Van Drunen,[3] in the determination of the thermal conductivity of liquids. However, it was Haupin,[4] who in 1960 first used this method to measure the thermal conductivity of ceramic materials. Nowadays the hot wire method is considered to be an effective and accurate means of determining the thermal conductivity of refractories. However, it is not possible to use this method for electricity conducting materials, unless some form of electrical insulation between the hot wire and the sample is developed.

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In the mathematical formulation of the method, the hot wire is assumed to be an ideal infinitely thin and long heat source which is embedded in an infinite surrounding material whose thermal conductivity is to be determined. Applying a constant electric current through the wire, a constant amount of heat per unit time and unit length is released by the wire and propagates throughout the material.

This propagation of heat throughout an infinite medium generates a transient temperature field, which has a logarithmic time dependence. In practice,[5] the theoretical infinite linear source is approached by the use of a very thin electric resistance and the infinite solid is replaced by a finite sample.

Four variations of the hot wire method are known.[6] The theoretical model is the same, and the basic difference among them lies in the temperature measurement procedure. In this work the variation known as hot wire parallel technique was employed. This technique was standardized in 1978 by DIN 51046 Standard—Part 2. The thermal conductivity is calculated according to the following equation:

$$k = \frac{-q'}{4\pi T(t)} E_i\left(\frac{-\rho c_p r^2}{4kt}\right) \qquad (1)$$

where:
k = thermal conductivity of the material (W/(m.K)), q' = linear power density (W/m), ρ = material bulk density (kg/m^3), c_p = specific heat of the material (J/(kg.K)), r = distance between hot wire and thermocouple (m), t = elapsed time after start of heat release (s), $T(t)$ = temperature rise registered by the thermocouple related to the initial reference temperature (K), $E_i(-x)$ = exponential integral function.

According to DIN 51046 Standard—Part 2, the thermal conductivity is determined at several selected pairs of times t and $2t$, by using eqn (1), and the values obtained are then averaged. In this work a different procedure is employed. The calculations, starting from the recorded temperature transient in the sample are carried out by using a non-linear least squares fitting method.[7] Both thermal conductivity and specific heat in eqn (1) are fitted in order to obtain the best possible approximation between the thermal transient experimentally registered and the one predicted by the theoretical model. In this case, these two thermal properties, thermal conductivity and specific heat are simultaneously determined from the same experimental temperature transient.

The thermal conductivity of a porous material containing water, displays a unique behaviour in the range from room temperature up to the temperature where the presence of water is no longer detected. So, it is believed to be very important to understand the quantitative effect that the amount of moisture contained in a porous material will have on the thermal conductivity. Taking into account this behaviour and its importance in some specific thermal calculations a numerical simulation model is proposed in this work. This model is able to estimate the effect of moisture content on the thermal conductivity of porous ceramic materials containing water inside their structure.

2 The simulation model

When using the hot wire technique to evaluate the thermal conductivity of a porous media containing adsorbed water, one is in reality taking into account, simultaneously, the heat transfer through the solid phase and the heat absorption by the liquid phase. Under these conditions the thermal gradient, which can be registered between two points inside the specimen, is different from that which would be expected in the absence of adsorbed water. The liquid water consumes part of the heat energy and may eventually vaporize, leading to a lower temperature profile, which means an increase in the experimentally measured thermal conductivity, considering that the technique uses the temperature transient established inside the material. Since the method assumes an infinitely long and thin heat source, the heat conduction inside the specimen is of a radial nature. We assume that the solid is composed of N concentric individual layers with radii r_i measured from the center of the specimen where the hot wire is embedded. Figure 1 illustrates this procedure.

An energy balance of the form of eqn (2) may be defined for each region:

$$\begin{aligned}&\left[\text{Heat flux in}\right]_i - \left[\text{Heat flux out}\right]_i = \\ &\left[\text{Rate of internal energy change}\right]_i\end{aligned} \qquad (2)$$

The presence of moisture can be taken into account if we add to the right hand side of eqn (2), the rate of internal energy change for the mass of water contained locally. As proposed by Bonacina
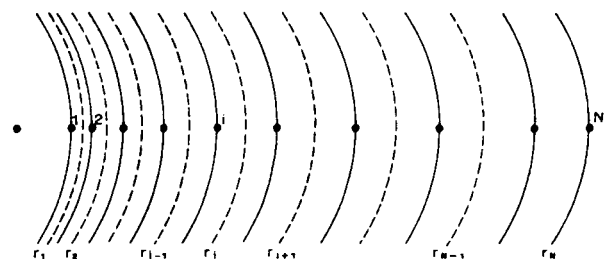

Fig. 1. Annular cylindrical regions for the numerical analysis.

et al.[8] for a solid–liquid transition, the change of state of the adsorbed water can be simulated through the inclusion in eqn (2) of an appropriate correction for the specific heat.

Then by applying the balance eqn (2) for each region we derive eqns (3), (4) and (5).

For $i = 1$:

$$q' + k2\pi(r_1 + \frac{r_2 - r_1}{2})\frac{\langle T_2 \rangle - \langle T_1 \rangle}{r_2 - r_1} = (\rho c + Cw(1)c_W(T_1)).$$

$$\pi\left[\left(r_1 + \frac{r_2 - r_1}{2}\right)^2 - \left(r_1 - \frac{r_2 - r_1}{2}\right)^2\right].\frac{T_1^{t+\Delta t} - T_1^t}{\Delta t}$$

(3)

For $i = 2, 3, \ldots, N - 1$:

$$k2\pi(r_i - \frac{r_i - r_{i-1}}{2})\frac{\langle T_{i-1} \rangle - \langle T_i \rangle}{r_i - r_{i-1}}$$

$$+ k2\pi(r_i + \frac{r_{i+1} - r_i}{2})\frac{\langle T_{i+1} \rangle - \langle T_i \rangle}{r_{i+1} - r_i}$$

$$= (\rho c + Cw(i)c_W(T_i))\pi\left[\left(r_i + \frac{r_{i+1} - r_i}{2}\right)^2\right.$$

$$\left. - \left(r_i - \frac{r_i - r_{i-1}}{2}\right)^2\right]\frac{T_i^{t+\Delta t} - T_i^t}{\Delta t}$$

(4)

For $i = N$:

$$k2\pi\left(r_N - \frac{r_N - r_{N-1}}{2}\right)\frac{\langle T_{N-1} \rangle - \langle T_N \rangle}{r_N - r_{N-1}}$$

$$= (\rho c + Cw(N)c_W(T_N)).\pi\left[r_N^2 - (r_N - \frac{r_N - r_{N-1}}{2})^2\right]$$

$$\frac{T_N^{t+\Delta t} - T_N^t}{\Delta t}$$

(5)

where:
q' = linear power density, k = solid thermal conductivity, ρ = solid density, c = solid specific heat, $Cw(i)$ = adsorbed water concentration at region i, $c_w(T_i)$ = specific heat of the water, which is a function of the temperature, on the region i, $\langle T_i \rangle$ = average temperature on the region i between times t and $t + \Delta t$, t = time and r_i = radius of the region i.

In order to facilitate the numerical calculations we introduce a dimensionless transformation for position, time and temperature, as shown in eqns (6)–(8).

$$r_i^* = \frac{r_i}{L_{ref}}$$

(6)

$$\tau = \frac{\alpha t}{L_{ref}}$$

(7)

$$\theta_i = \frac{T_i - T_{rt}}{T_{ref}}$$

(8)

where:
L_{ref} = reference linear dimension (distance between hot wire and thermocouple), $\alpha = \frac{k}{\rho c}$ = thermal diffusivity of the solid, T_{rt} = room temperature, T_{ref} = reference temperature (water vaporization temperature), r_i^* = dimensionless radius of the region i, τ = dimensionless time and θ_i = dimensionless temperature of the region i.

If we take as the dimensionless average temperature for each region, the arithmetic mean of the temperatures between instants t and $t + \Delta t$, we can write eqns (9)–(11).

$$\langle \theta_{i-1} \rangle = \frac{\theta_{i-1}^{t+\Delta t} + \theta_{i-1}^t}{2},$$

(9)

$$\langle \theta_i \rangle = \frac{\theta_i^{t+\Delta t} + \theta_i^t}{2},$$

(10)

$$\langle \theta_{i+1} \rangle = \frac{\theta_{i+1}^{t+\Delta t} + \theta_{i+1}^t}{2}$$

(11)

The specific heat of water $c_w(\theta_i)$ in region i is then given by eqn (12).

$$c_w(\theta_i) = \begin{cases} c_L & \text{if} & \theta_i < \theta_{FT} - \frac{\Delta\theta}{2} \\ \frac{h_{LV}}{\Delta\theta T_{ref}} + \frac{c_L + c_V}{2} & \text{if} & \theta_{FT} - \frac{\Delta\theta}{2} < \theta_i < \theta_{FT} + \frac{\Delta\theta}{2} \\ c_V & \text{if} & \theta_i > \theta_{FT} + \frac{\Delta\theta}{2} \end{cases}$$

(12)

where:
c_L = specific heat of the liquid water, c_V = vapour specific heat, h_{LV} = water vaporization entalpy, θ_{FT} = dimensionless temperature of phase transition and $\Delta\theta$ = dimensionless temperature interval for phase transition.

The heat flux originating from the hot wire may promote the vaporization of the adsorbed water and consequently the creation of pores. In this manner, the liquid content in each region changes with time, as well as the level of porosity left behind by the water driven off. Therefore, the water content $Cw(i)$, in eqns (3), (4) and (5) will have to be corrected as shown in eqn (13).

$$Cw(i, t) = Cw(i, t - \Delta t) - \frac{M_{ev}(i, t - \Delta t)}{V(i)}$$

(13)

where:
$Cw(i, t)$ = water content in the region i, at the instant t, $Cw(i, t - \Delta t)$ = water content in the region i, at instant $t - \Delta t$, $M_{ev}(i, t - \Delta t)$ = mass of water that evaporates from the region, i at the instant $t - \Delta t = \{Cw(i, t - \Delta t)V(i)[\theta_i^t - \theta_i^{t-\Delta t}]T_{ref}[c_w(\theta_i^t) - c_L]\}/h_{LV}$, $V(i)$ = volume of region i.

The bulk solid thermal conductivity can also be corrected for the changing level of porosity by

means of the simplified Loeb's equation[9] as shown in eqn (14).

$$k(i, t) = k_s(1 - P(i, t - \Delta t)) \qquad (14)$$

where:
$k(i, t)$ = thermal conductivity of the porous solid phase of region i, at instant t, k_s = thermal conductivity of the solid phase without pores, and $P(i, t - \Delta t)$ = porosity of the region i, at instant $t - \Delta t$, and is given by:

$$P(i, t - \Delta t) = \frac{1}{\rho_{lw}} \sum_{\substack{j = t - \Delta t \\ j = n\Delta t}} \frac{M_{\text{ev}}(i, j)}{V(i)} \qquad (15)$$

$$n = 0, 1, 2 \ldots$$

where ρ_{lw} = liquid water density.

It has to be pointed out that the porosity term in eqn (14), represents only the pores created by the adsorbed water driven off, neglecting in this analysis the inherent porosity already present in the specimen. In this way the term k_s in eqn (14), becomes the thermal conductivity of the bulk solid phase when the porosity created by the water driven off is neglected. Combining eqns (3)–(15), and after some algebraic simplifications, we can write the final result in a matrix form, as expressed by eqn (16).

$$B^K \theta^{K+1} = C^K \theta^K + D \qquad (16)$$

where:
θ = column matrix of dimensionless temperatures, B and C = square matrices of dimensionless temperature coeficients terms, and the superscripts K and $K + 1$ refer to the times t and $t + \Delta t$.

To the temperature profile generated by eqn (16), we can apply a non linear regression analysis procedure which is used to evaluate the thermal conductivity by the hot wire technique. It is then possible to obtain a numerical value for the thermal con-ductivity of the system solid phase/adsorbed water and to compare it with the one for the dried material.

When the electric current passes through the hot wire, a constant amount of heat, per unit time and per unit lenght is released by the wire and propagates throughout the material. The liquid water consumes part of this energy and may eventually vaporize. As the reference temperature increases, the amount of water that may vaporize also increases. As a consequence of this energy absorption by the water, the temperature rise as a function of time registered by the thermocouple at a fixed distance from the hot wire is less than that which would be registered if the porous material was free of water. This phenomenom means in practice a thermal conductivity increasing with temperature. However, as the reference temperature increases toward higher values, the adsorbed water is driven off, and this phenomenom promptly creates two factors that contribute for a decrease in the thermal conductivity: less availability of water to absorb the heat released by the hot wire, and an increase in the porosity due to water evaporation.

The combination of these mechanisms which have opposite effects, i.e. absorption of heat by adsorbed water, and pores formation due to the evaporation of the same water, results in the thermal conductivity of a moist porous ceramic material as a function of temperature to reach a maximum value. After this maximum value the pores formation mechanism predominates and the thermal conductivity decreases as temperature increases, as shown in Fig. 3.

3 Results and conclusions

With the purpose of checking the numerical simulation model proposed in this work, it was evaluated the thermal conductivity of a hypothetical porous ceramic material containing different
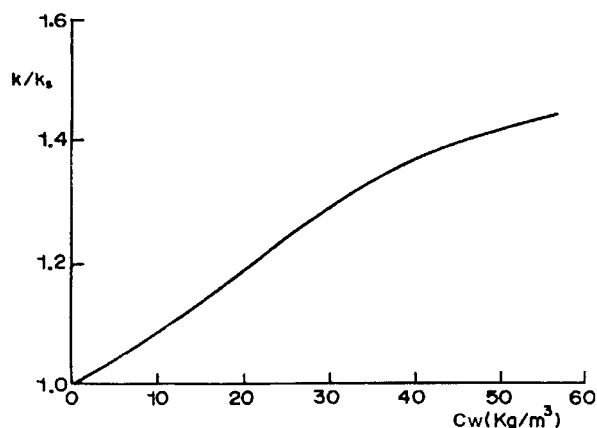
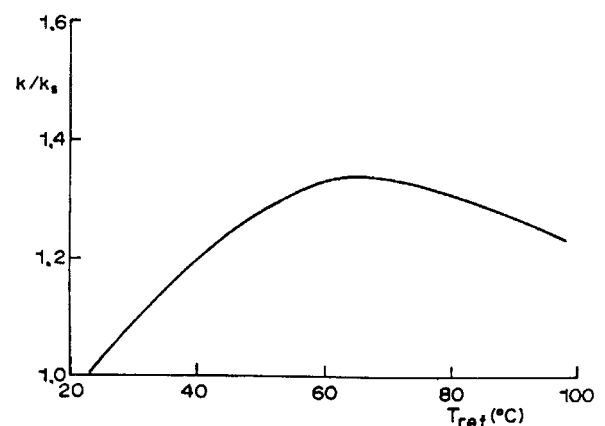**Fig. 2.** Ratio k/k_s as a function of water concentracion C_w.

Fig. 3. Ratio k/k_s as a function of temperature.

concentrations of water in its structure. Calculations were carried out for a reference temperature of 70°C and linear power density at $r = 0$ of 190 W/m. Results of this simulation are shown in Fig. 2, where k is the thermal conductivity predicted with the simulated thermal transient, and k_s is the thermal conductivity of the material solid phase.

Through Fig. 2 it can be seen that the thermal conductivity of a porous ceramic material is highly sensitive to the amount af adsorbed water contained in its structure. This result was already expected, since increasing the concentration of adsorbed water, also increases the amount of heat to be absorbed, and the temperature gradient across the material decreases, meaning, in practice, a thermal conductivity larger than one that would be measured for the dry material.

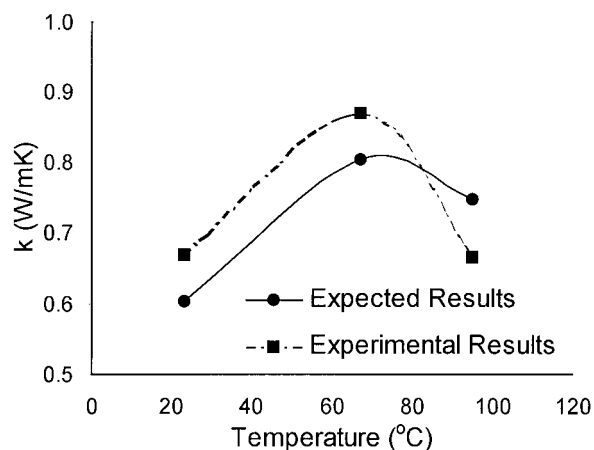This behaviour of the thermal conductivity versus temperature as foreseen by this proposed numerical simulation model was actually experimentally measured for an unfired refractory concrete,[10] as shown in Fig. 4.

Fig. 4. Thermal conductivity: expected and experimental results.

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