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Effect of moisture and porosity on the thermal properties of a conventional refractory concrete

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Abstract

An investigation was carried out to study the effect of moisture and porosity on the thermal conductivity, thermal diffusivity and specific heat of a conventional aluminous refractory concrete. The experimental technique employed was the hot wire parallel technique, and measurements were carried out from room temperature up to 1000 °C. The thermal conductivity and the specific heat were simultaneously determined from the same experimental thermal transient, and the thermal diffusivity was derived from these two properties. A 60 wt.% alumina grog and a 60 wt.% alumina calcium aluminate cement were the raw materials employed in this work. Five different porosity levels were obtained by proportioning three different aggregate grain sizes. Experimental results show a drastic influence of the moisture content on the thermal conductivity of the refractory concrete, doubling its value when compared with the same fired composition, depending on the temperature range considered in the measurements. It was also observed for the fired material, a smooth variation of the thermal conductivity with the temperature for each composition in the temperature range studied, and a modified form of the Loeb equation was employed to evaluate the thermal conductivity of the fully dense solid. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Steps taken in order to rationalize energy consumption became procedures of fundamental importance in recent years. So, heat transfer with the maximum possible efficiency by using adequate materials is as important as avoiding heat losses. The knowledge of materials physical properties is very important in all engineering projects. However, in the case of high temperature working conditions, thermophysical properties assume a fundamental role, since accurate heat transfer calculations must be taken into account.

Thermal conductivity, thermal diffusivity and specific heat are the three most important physical properties of a material that are needed for heat transfer calculations. The equation relating these properties is given by:

$$\alpha = \frac{k}{\rho c_p} \tag{1}$$

where: α = thermal diffusivity (m^2/s), k = thermal conductivity [W/(m.K)], ρ = bulk density (kg/m^3), c_p = specific heat [J/(kg.K)].

Thermal conductivity is the property that determines the working temperature levels of a material. It assumes a critical role in the performance of refractory materials in high temperature applications, and it is an important parameter in problems involving steady state heat transfer. It is one of the physical quantities whose measurement is very difficult and it requires high precision in the determination of the factors necessary for its calculation. The specific heat (heat capacity per unit mass) is also a decisive property of ceramic materials in high temperature applications. Thermal diffusivity is a measure of rapidity of the heat propagation through a material. It is an important property in all problems involving non-steady state heat conduction.

The thermal conductivity of porous ceramic materials displays a singular behaviour when moisture is present in its structure. Recently, Santos and Cintra[1] proposed a numerical simulation model which permits a quantitative evaluation of the effect of moisture on the thermal conductivity of porous ceramic materials. Santos[2] also

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reported data concerning the effect of moisture on the thermal conductivity and specific heat of Portland castables with different aggregates, but for applications at relatively low temperatures, up to 250 °C.

The presence of moisture may affect material thermophysical properties in two different situations: when the humidity level varies in the working environment, and in the first heating up schedule of monolithic refractories, because of its inherent transitional nature before being fired.

Nowadays, refractory concretes correspond to a large fraction of all refractory materials sold worldwide. Their lower thermal conductivity, permitting thinner linings or improving thermal efficiency may be cited as one of the most important, among the various advantages in the usage of this kind of material, when compared with conventional refractories. However, refractory concretes have a transitional nature considering that their microstructure changes as a function of temperature and time, as a consequence of the loss of adsorbed and water of crystallization, in addition to the reactions between the cement and the fine aggregates. So, one can expect drastic changes in the thermal properties during this transition period (in practice, the first heating up schedule), notably because water is driven off, and new phases and microcracks nucleate in the matrix.

In this work the effect of moisture and porosity on the thermal conductivity, thermal diffusivity and specific heat of a conventional aluminous refractory concrete was investigated. The experimental technique employed was the hot wire parallel technique and the calculations were carried out by using a non linear least squares fitting method. The temperature range of measurements was from room temperature up to 1000 °C, for the unfired and fired material. Thermal conductivity and specific heat were simultaneously determined from the same experimental thermal transient, and thermal diffusivity was derived from these two properties with the aid of Eq. (1).

2. Sample preparation

The raw materials employed were a 60 wt.% alumina grog proportioned in the ($-3+6$), ($-50+80$) and (-140) mesh sizes as aggregate, and a 60 wt.% alumina calcium aluminate cement.

The aggregate and cement were then weighed and mixed with the appropriate amount of water to give the desired consistency. The ball-in-hand test was used to determine the satisfactory water addition.

Samples in the shape of bricks, having dimensions 230×112×59 mm were prepared by vibrating the moist mass.

A steel mould was employed, and five samples were then cast simultaneously. A good surface is important to ensure that the two bricks used in the hot wire technique are in good thermal contact with each other and the heater wire.

Five sets of samples denominated A1, A2, A3, A4 and A5 were prepared using a fixed amount of cement. The moulded samples were then covered with a wet cloth and left to stand at room temperature under a 75% relative humidity for a period of 24 h. After this step the samples were demoulded and cured under a 95% relative humidity for 24 h. In the next step the samples were left at room temperature for 24 h, dried at 110 °C for 2 h, and left to stand again at room temperature under 75% relative humidity for 15 days, and then they were ready to be tested. Details of the samples are given in Table 1.

Sample bulk density was obtained from mass and volume measurements, and the volume fraction of open porosity was determined according to ASTM C 20 standard.

3. Experimental technique

The experimental technique employed in this work was the hot wire parallel technique. 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 an effective and accurate means of determining the thermal conductivity of refractories.

In the mathematical formulation of the method, the hot wire is assumed to be an ideal infinitely thin and long heat source which is 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, generating a transient field of temperatures. In practice,[5] the theoretical infinite linear source is approached by a thin electric resistance and the infinite solid is replaced by a finite sample.

Table 1
Sample details

Sample	Aggregate grain size distribution (wt.%)			Cement (wt.%)	Bulk density (kg/m^3)	Open porosity (%)
	($-3+6$)	($-50+80$)	(-140)			
A1	–	–	85	15	1660	36.37
A2	20	10	55	15	1790	32.31
A3	10	70	5	15	1960	21.36
A4	20	50	15	15	2080	20.96
A5	70	10	5	15	2190	17.13

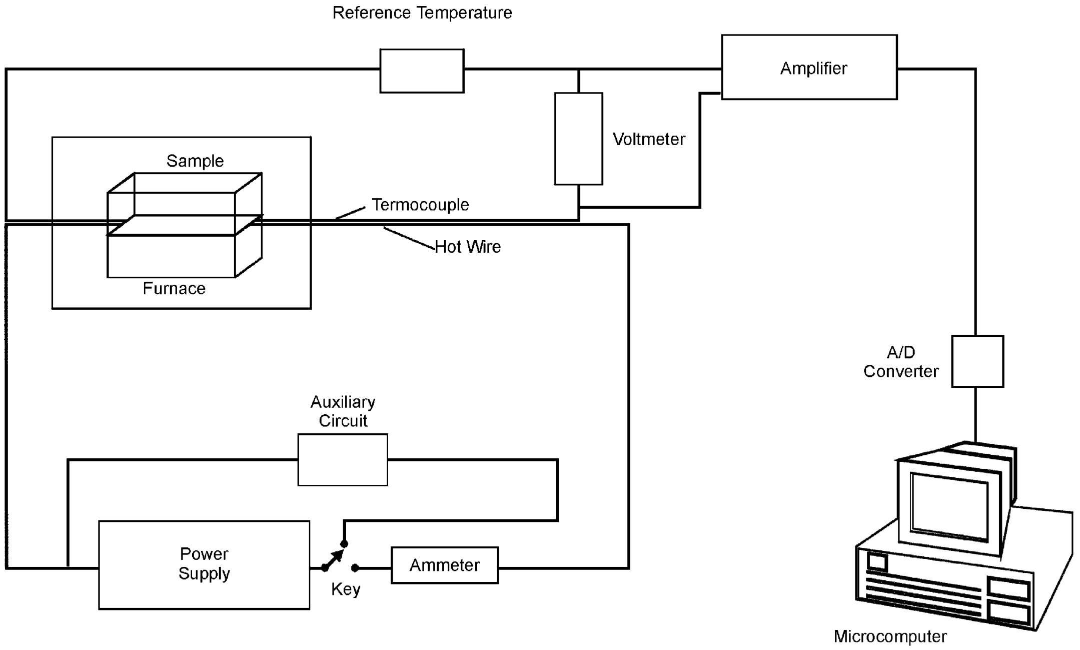

Fig. 1. Hot wire parallel technique apparatus.

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

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

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 beginning 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.

A schematic diagram of the apparatus is shown in Fig. 1.

According to DIN 51046—Part 2 Standard, the thermal conductivity is determined at selected times, by using Eq. (2), and the several values obtained are then averaged. In this work a different procedure is adopted. The calculations, starting from the recorded temperature transient in the sample are carried out by using a non-linear least squares fitting method.[7] So, all the points of the experimentally registered thermal transient are considered in the calculations. Both thermal conductivity and specific heat in Eq. (2) are fitted in order to obtain the best possible approximation between the thermal transient experimentally registered and that 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 transient. Thermal diffusivity is then calculated by using Eq. (1). So, using the same apparatus is possible to determine these three thermal properties in the same experiment.

4. Results and discussions

Measurements were carried out from room temperature up to at approximately 1000 °C, in 100 °C intervals.

Figs. 2, 3 and 4 show the thermal conductivity, specific heat, and the derived thermal diffusivity according to Eq. (1), as a function of temperature for the unfired material. After the first heating up schedule, samples were fired for 6 h at 1000 °C, and then, measurements were carried out for the fired concrete, using the same temperature intervals. The thermal conductivity and specific heat data obtained are plotted in Figs. 5 and 6 as a function of temperature. In Fig. 7 the derived thermal diffusivity data are also presented.

Through Fig. 2, it can be seen that there is a common trend for all samples concerning the temperature dependence of the thermal conductivity. It is also apparent that three different regions can be identified in each plot.

Region 1 displays an increase in the thermal conductivity, from room temperature up to approximately 60 °C. At this point a maximum is apparently attained. Region 2 starts at about 60 °C with a steep decrease in

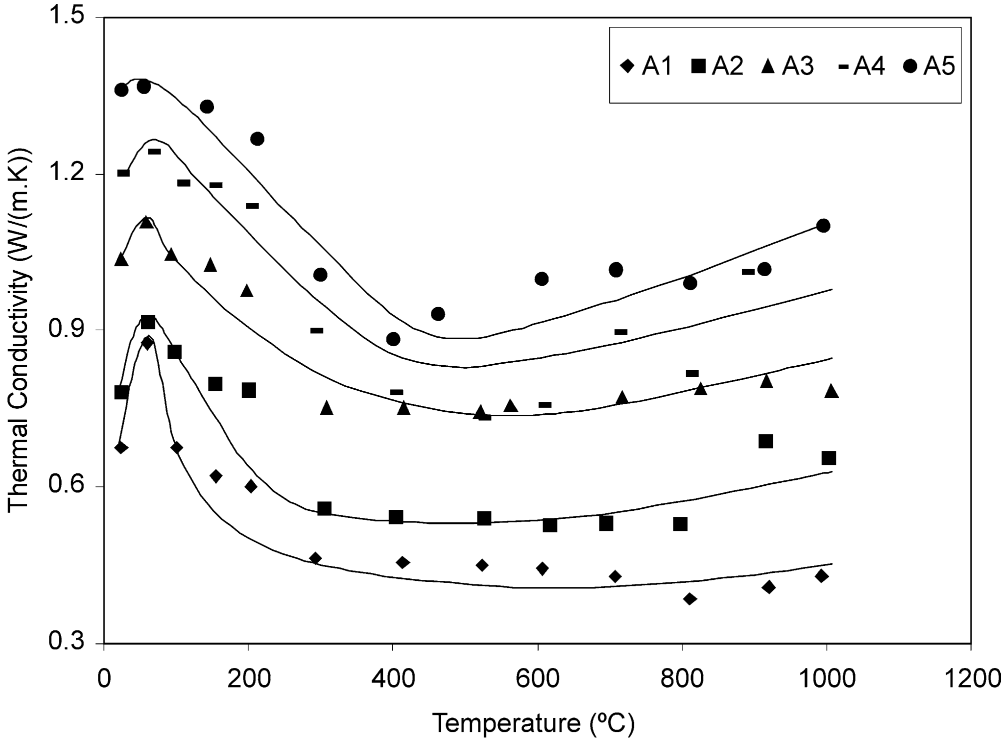

Fig. 2. Thermal conductivity as a function of temperature-first heating up.

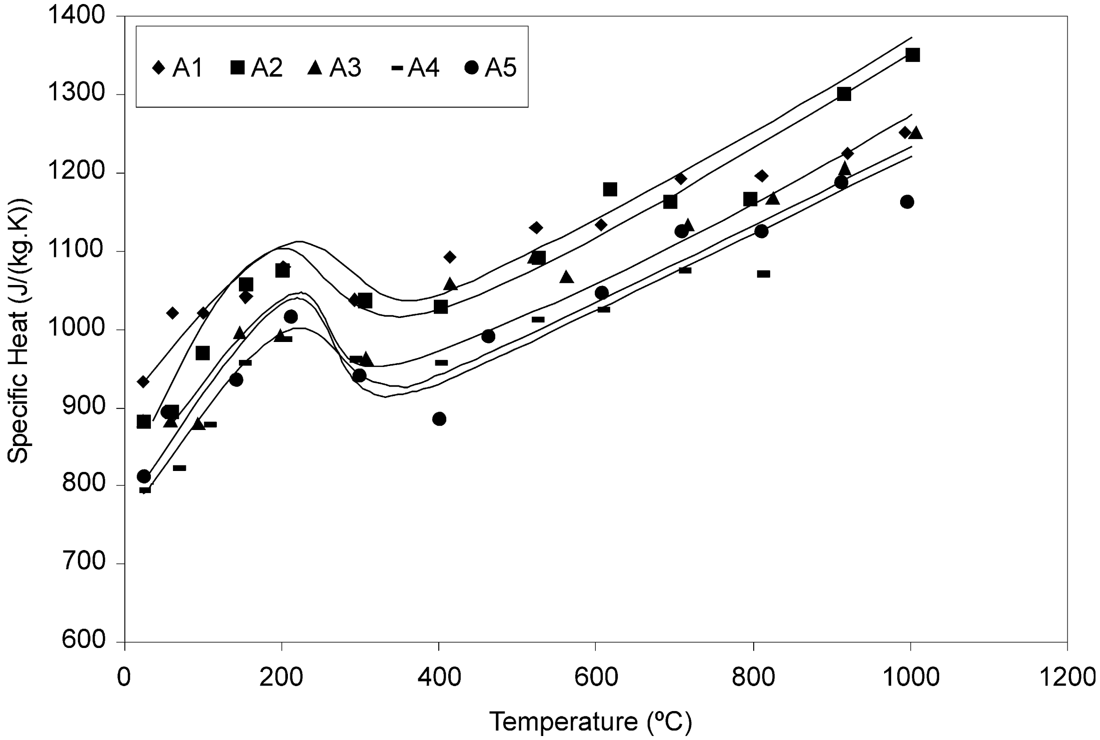

Fig. 3. Specific heat as a function of temperature-first heating up.

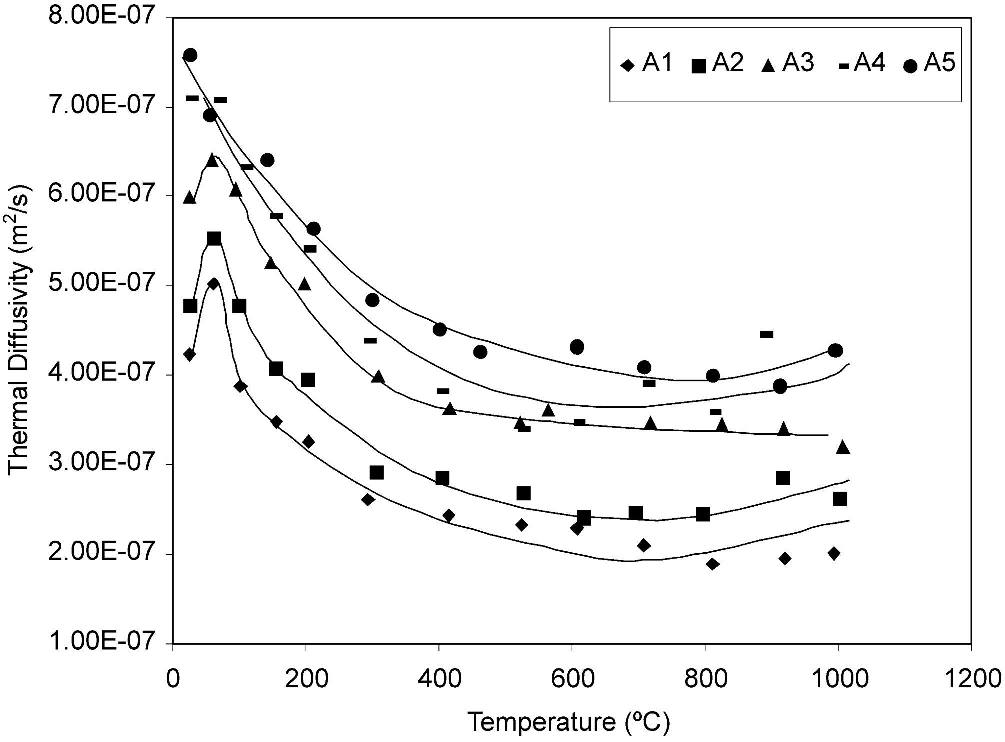

Fig. 4. Thermal diffusivity as a function of temperature-first heating up.

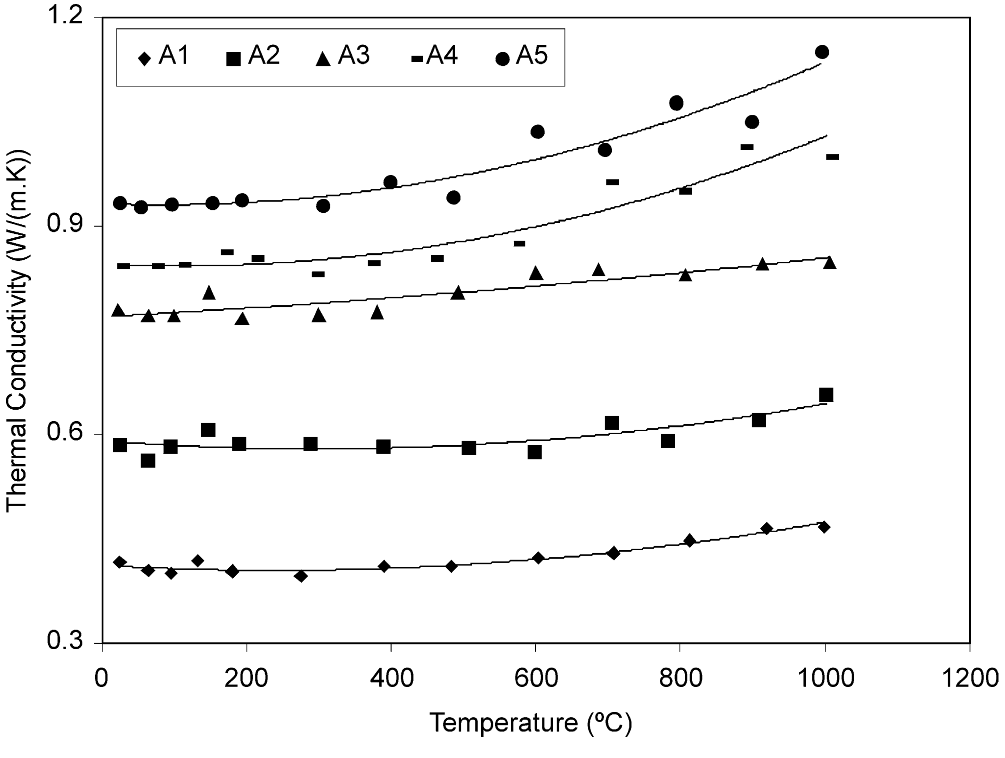

Fig. 5. Thermal conductivity as a function of temperature.

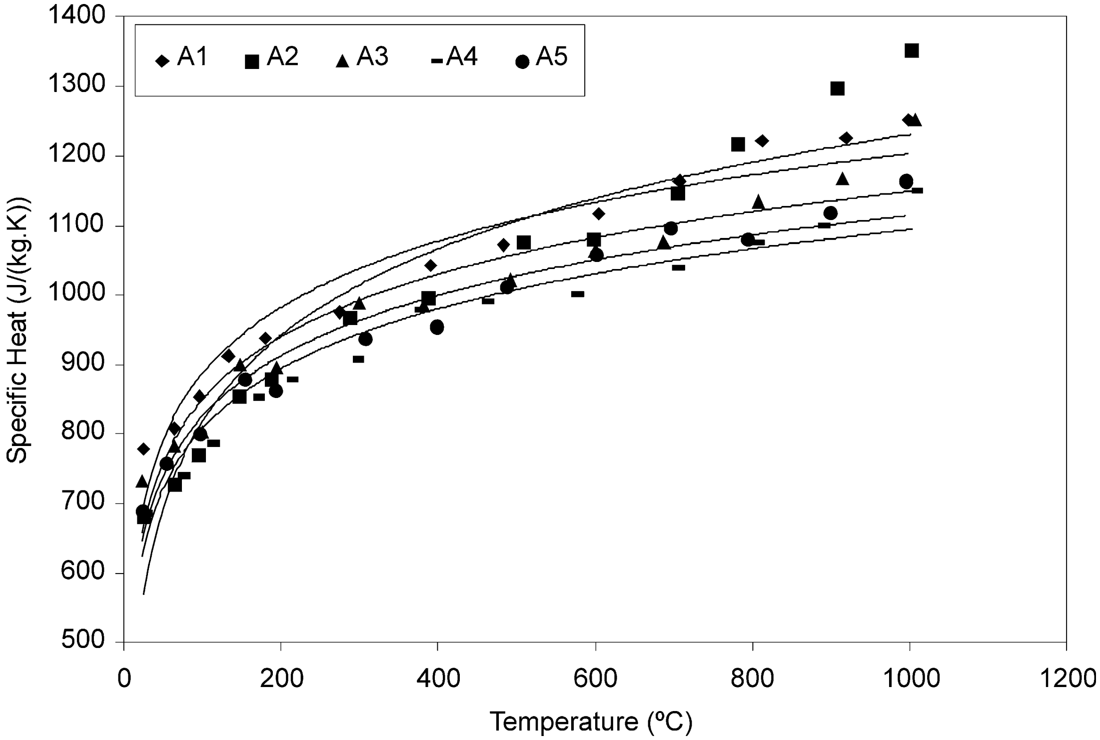

Fig. 6. Specific heat as a function of temperature.

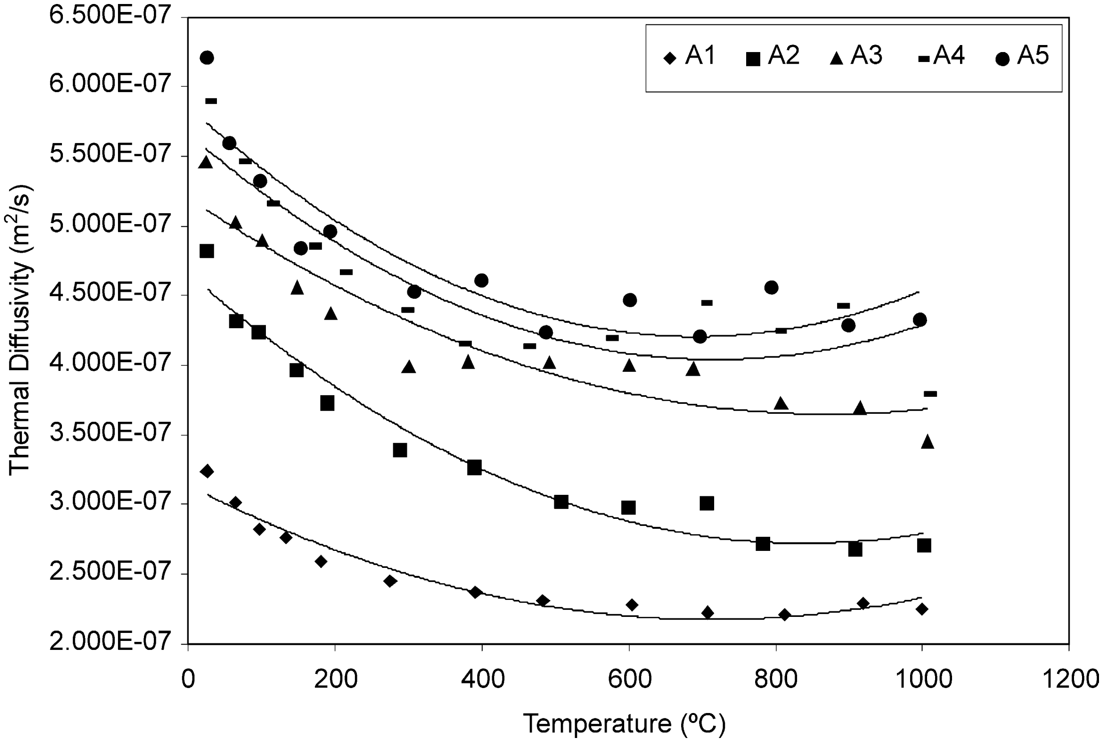

Fig. 7. Thermal diffusivity as a function of temperature.

thermal conductivity which ends close to 500 °C. At this point a minimum is apparently attained. Region 3 is represented by the gradual increase in thermal conductivity, from around 500 °C, and this behaviour is typical of fired refractories of the same class.

The trend in region 1 can be explained in terms of the adsorbed water that absorbs part of the heat generated by the electric current passing through the hot wire. The consequence of this absorption of heat by the water is that the temperature rise at a fixed distance from the hot wire is less than the one that would be observed if water was not present. This effect in practice leads to an effective increase in the experimentally measured thermal conductivity. In addition, the more pores the specimen has at start up, the more water it adsorbs, and the steeper is the increase in k from room temperature up to approximately 60 °C. As the temperature increases beyond 60 °C, the amount of adsorbed water decreases (the phase transition from liquid to gaseous state occurs around 100 °C), leaving empty spaces behind, which contribute to the observed decay in thermal conductivity.

The decrease of k in region 2 can be linked to the loss of 4.5 water molecules from the 6 initially present in the aluminous cement hydrated phase C_3AH_6. This phenomenon readily occurs between 200 and 300 °C which was confirmed by DTA. As this crystallization water is lost, the porosity increases and microcracks may be nucleated in the matrix phase. The combination of these two effects turns out to be a very effective heat transfer barrier, resulting in a further decrease in the thermal conductivity. The minimum in the thermal conductivity occurs at lower temperatures for the less porous specimens. This fact can be linked to the densification occurring as a result of the reaction between the cement and the fine aggregate fraction, which is easier to happen when the particles are closer together, i.e., when the material has initially less porosity.

The behaviour of the thermal conductivity in region 3 which starts at the point of minimum can be related to the contribution of three mechanisms: densification (sintering), radiation contribution and vitreous phase contribution. The contribution of densification is self evident, since the main effect is the decrease in porosity and as a result the solid phase becomes more continuous.

The vitreous phase inherently present in the aggregates, in addition to the one formed during the reaction between the cement and the fine aggregates, contributes to an increase in thermal conductivity, since for the vitreous phase the thermal conductivity is proportional to the specific heat which increases with temperature. A simulation model was also proposed by Santos and Cintra.[1] to analyse quantitatively the effect of moisture content on the thermal conductivity of porous ceramic materials.

It also can be seen from Fig. 2 that the higher is the porosity level, the higher is the thermal conductivity peak around 60 °C. For samples with larger porosities the amount of adsorbed water in its structure is also larger. As a consequence, the amount of heat absorbed during the measuring process is larger when compared with a sample with a lower amount of water, resulting in a lower temperature rise in the measuring point, which means in practice a lower thermal conductivity experimentally measured. So, a certain proportionality is expected concerning the thermal conductivity peak dependence with the sample porosity. Fig. 8 shows the plot of the ratio peak thermal conductivity to the room temperature thermal conductivity as a function of the inverse of density. The parameter R^2 shows that the experimental results obtained are in excellent agreement with this proposed assumption.

Fig. 3 also displays a common trend for all samples concerning the temperature dependence of the specific heat. This fig. shows an increase in the specific heat from room temperature up to approximately 200 °C. At this point a maximum is apparently attained, and starting from this point the specific heat decreases with temperature rise attaining a minimum value around 320 °C, and then, it gradually increases with temperature raise.

The behaviour of the specific heat may be also explained in terms of adsorbed water. The specific heat of water is 4 or 5 times the specific heat of a ceramic material. So, the specific heat of the compound material (solid material + water contained inside the pores) is increased in the temperature range where water is present. As adsorbed and crystallization water is eliminated by evaporation as the temperature is raised, the specific heat decreases from its maximum value at 200 °C, to its minimum value at approximately 320 °C, and then it gradually increases with temperature rise as predicted by Debye theory of specific heat.[8]

Since both thermal conductivity and specific heat are significantly affected by presence of moisture, and thermal diffusivity is derived from these properties, its behaviour as a function of temperature is also dependent of the moisture content as shown in Fig. 4.

During the first heating up schedule various microstructural changes occur as a function of temperature and time: water is driven off, pores are created and new phases and microcracks nucleate in the matrix. After this step samples were fired at 1000 °C for 6 h, and then, the behaviour of the thermal properties of the fired refractory concrete becomes similar to those of common refractory materials.

As expected, Fig. 5 clearly shows a systematic trend of increasing conductivity with the decreasing porosity level. On the same fig. in the temperature range studied there can be seen a smooth variation of the thermal conductivity with the temperature for each porosity level.

For pure crystalline materials, when temperature increases, specific heat also increases to an approximately

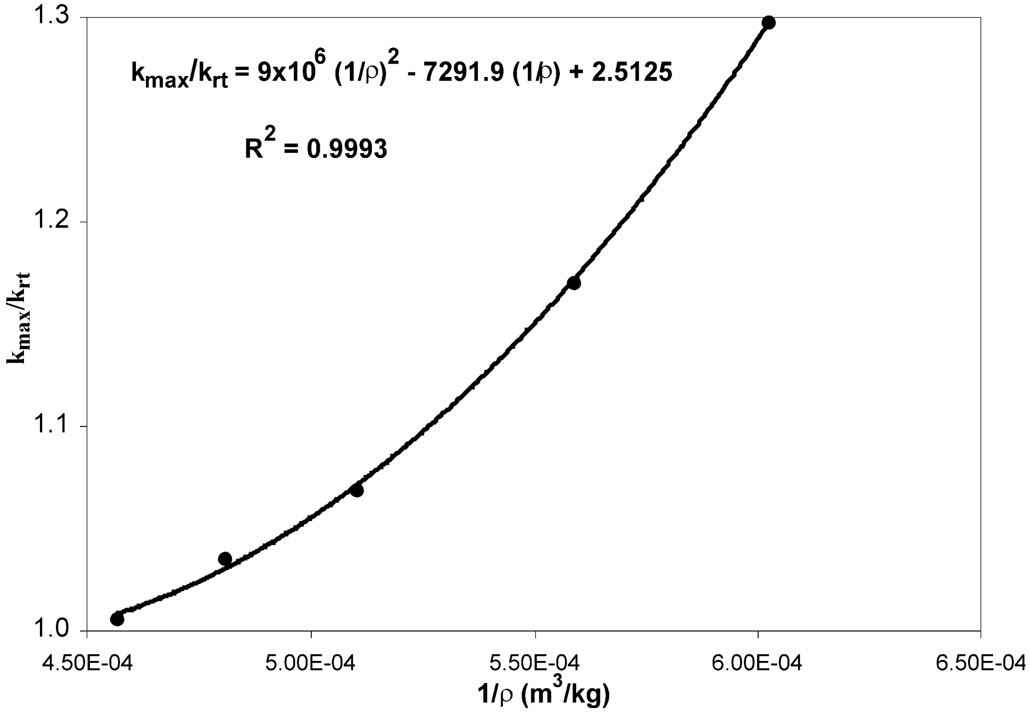

Fig. 8. Peak thermal conductivity as a function of density.

constant value and the phonons mean free path decreases, since it is proportional to $1/T$. The net effect is a decrease in the thermal conductivity. Experimental results indicate that for pure crystalline materials,[8,9] the thermal conductivity may be represented by an equation of the form:

$$k = A/T + B \tag{3}$$

where k = thermal conductivity, T = absolute temperature, and A, B = experimental constants to be determined.

For glasses, the mean free path may be considered approximately constant, and when temperature increases, the thermal conductivity increases in proportion to the specific heat. In this case, the thermal conductivity may be represented by an equation of the form:[8,9]

$$k = CT + D \tag{4}$$

where C and D are also experimental constants to be determined.

If a material is a combination of crystalline and glassy phases, the temperature dependence of the thermal conductivity may be represented by the equation:[8,9]

$$k = \frac{1}{AT + B + \frac{C}{T}} \tag{5}$$

where A, B and C are also experimental constants to be determined.

The behaviour of the thermal conductivity shown in Fig. 5 is that one predicted by Eq. (5). When the experimental results are fitted to this equation, for each porosity level, all the correlation coefficients are higher than 0.97.

For ceramic materials the heat capacity increases with the temperature, starting from a low value at low temperatures, and approaching the value 6 M cal/(mol.K) at high temperatures, where M is the number of atoms per mole. Specific heat is defined as heat capacity per unit mass. Fig. 6 shows that the results obtained for the fired refractory concrete are those predicted by Debye theory of specific heat.[8] As a consequence, the thermal diffusivity (Fig. 7) does not exhibit any special feature, and also has a typical behaviour of a material containing both crystalline and glassy phases.

Many models are available to predict the thermal conductivity of two-phase systems in terms of the thermal conductivities of the constituents. These are too numerous to detail, and have been reviewed in several occasions. In situations where the second phase is porosity it is a common practice to set its thermal conductivity to zero, whereupon some of the analyses to

Table 2
Results of best fit to equation $k_p = k_s(1 - \beta P)$

T (°C)	k_s (W/mK)	β	R
65	1.361541	1.923026	0.989848
200	1.365131	1.890478	0.981666
400	1.388707	1.921634	0.984970
600	1.506552	1.971366	0.991333
800	1.567564	1.975027	0.982649
1000	1.683706	1.727465	0.978992

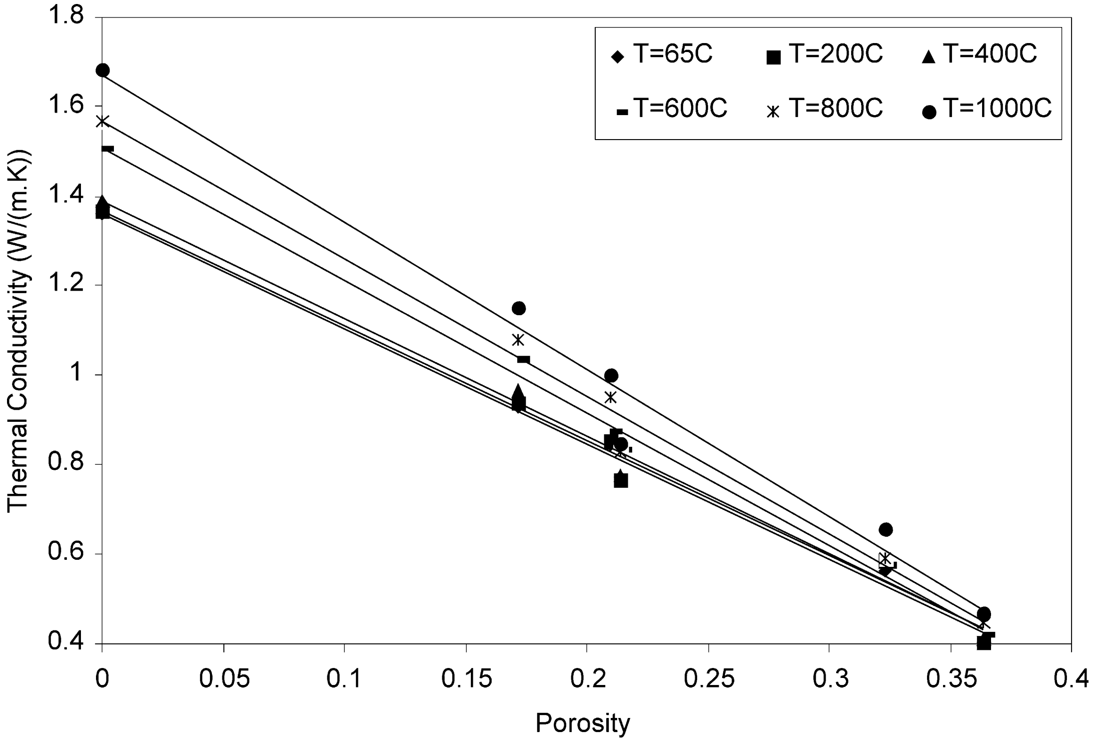

Fig. 9. Thermal conductivity as a function of porosity.

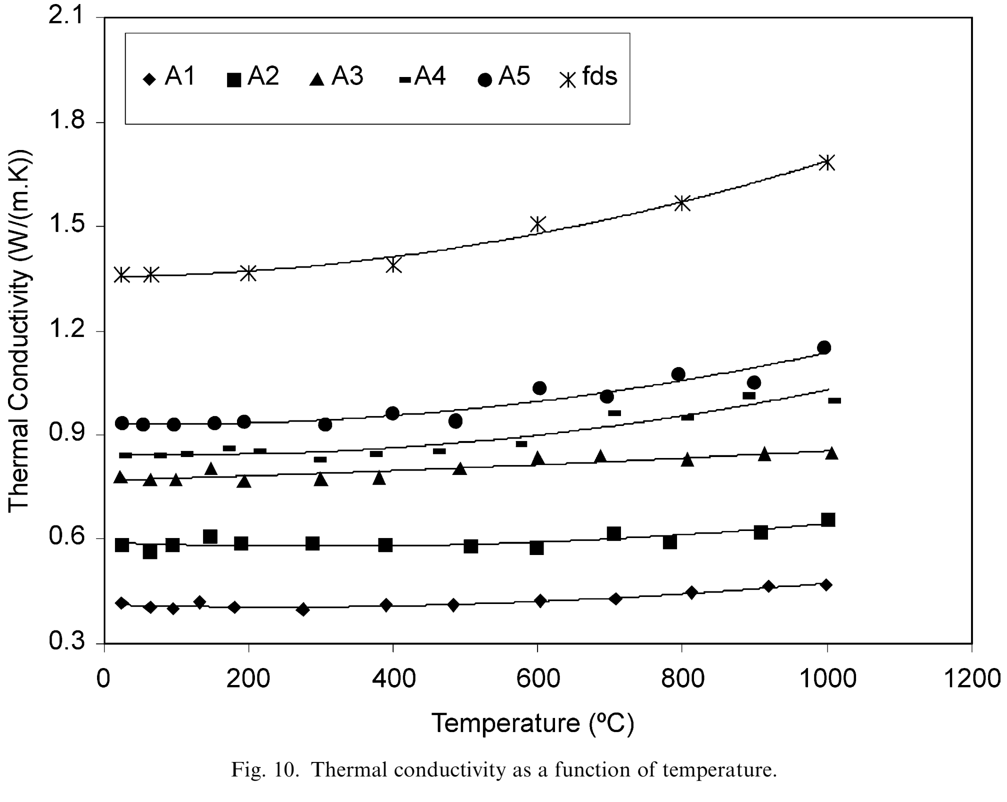

Fig. 10. Thermal conductivity as a function of temperature.

predict thermal conductivity of two-phase systems revert to a simpler form. The two equations most commonly used to describe the effect of porosity on the thermal conductivity are:

$$k_p = \frac{k_s(1-P)}{1+0.5P} \tag{6}$$

and

$$k_p = k_s(1-\beta P) \tag{7}$$

where k_p is the thermal conductivity at porosity P, k_s is the thermal conductivity of the fully dense solid, and β is a multiplicative factor.

Eq. (6) is a derivation of the Maxwell equation[10] whereby the conductivity of the second phase is set equal to zero. Eq. (7), a modified form of that due to Loeb[11] is, however more usually employed and the value for the parameter β depends on the geometry of the porosity and its orientation with respect to the direction of heat flow.

Eq. (7) predicts a linear dependence of the thermal conductivity with the porosity. So, the thermal conductivity of the solid material and the parameter β are simultaneously determined by regression analysis and the results are shown in Table 2 and Fig. 9. Fig. 10 shows the thermal conductivity of the fully dense solid (fds), i.e. for $P=0$, evaluated with the aid of Eq. (5), as a function of temperature together with the plots of Fig. 1.

It has been found[12] that values in the range $1<\beta<4$ have been determined for UO2 and this difference is attributed to microstructure and pore morphology. It has been further postulated that β is also temperature dependent. Considering the data in Table 2, it is clear that the values obtained for β are slightly temperature dependent. Santos and Taylor[13] have found the same dependence for the parameter β for alumina. For this material the values found ranged from 2.10470 and 1.93221.

5. Conclusions

The hot wire parallel technique is a suitable method for measuring the thermal conductivity of refractory materials. With this technique it is possible to measure thermal conductivity up to 25 W/(m.K), covering most commercial refractories. An advantage of the hot wire technique is the small temperature gradient across the sample, in the procedure of measurement, meaning that the thermal conductivity is calculated for a specific temperature. In the calorimetric techniques there is a considerable temperature gradient between the hot and cold faces of the sample. In this case the thermal conductivity evaluated must be referred as a "mean value" over the temperature gradient. An ideal technique would be that one that would require no temperature gradient across the sample and would be usable at low temperatures.

Since in the procedure adopted in this work thermal conductivity and thermal diffusivity are simultaneous determined, the thermal diffusivity is promptly derived. This is another advantage of this technique, since the three most important thermal properties are simultaneously determined in the same experiment.

The modified Loeb equation is very simple and useful to derive the thermal conductivity of a fully dense solid ($P=0$). β Values calculated are in agreement with those found in literature, showing the validity of this procedure.

It was shown that the amount of water has a drastic influence on the thermal conductivity of the unfired concrete. As higher is the material porosity level as bigger is the influence of the water, since in this case bigger is the content of water in its structure. For temperatures below 200 °C the ratio thermal conductivity of unfired material to the thermal conductivity for the fired material, for the same sample, and at the same temperature may be bigger than 2. It is believed that the knowledge of this behaviour is very important in many engineering projects.

Acknowledgements

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