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Experimental investigation of the effect of moisture on thermal conductivity and specific heat of porous ceramic materials

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Thermal conductivity and specific heat of porous ceramic materials display a unique behaviour when moisture is present in their structure. When compared with the corresponding dried materials, these properties are drastically altered, and the magnitude of these changes depends on the moisture content. In this work it was experimentally investigated the effect of adsorbed water on the thermal conductivity and specific heat of the most commonly structural material: castables and concrete of Portland cement. The experimental technique employed was the hot wire parallel technique, and measurements were carried out from room temperature up to 300°C during the heating and cooling cycle. The thermal conductivity and the specific heat were simultaneously determined from the same experimental thermal transient. Experimental results show a drastic influence of the adsorbed water on the thermal conductivity and specific heat of green castables. It was also observed that the addition of glassy phase on sample composition decreases the thermal conductivity and promotes the inversion of the slope of the curve thermal conductivity versus temperature for the dried material. © *2000 Kluwer Academic Publishers*

1. Introduction

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:

$$\alpha = \frac{k}{\rho c_{\mathrm{p}}} \tag{1}$$

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 assumes a critical role in the performance of refractory materials in high temperature applications. Low thermal conductivity values are required when the purpose is to minimize heat losses. On the other hand, when heat transfer from one site to another is desirable, refractories with higher thermal conductivities must be chosen. So, reliable thermal conductivity values are essential in a selection of a refractory in order to get the best performance of this material in a specific application.

Thermal conductivity is the property that determines the working temperature levels of a material, and it is an important parameter in problems involving steady state heat transfer. However, is one of the physical quantities whose measurement is very difficult and it requires high precision in the determination of the parameters envolved on its calculation.

The specific heat (heat capacity per unit mass) is also a critical property of ceramic materials in high temperature applications. It is a thermodynamic quantity, that is relatively simple to be determined for small and homogeneous samples. However, for heterogeneous materials having coarse grains or large pores such as refractories, where the quantity to be measured is the specific heat of the bulk of the body, including all present phases, and in this case being impossible the preparation of a small and representative sample, the measurement of this property must become particularly troublesome.

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.

A strong increase in the development and usage of ceramic materials has been noticed in the last decade. An inherent characteristic of a ceramic material is its porosity, sometimes desirable as in the case of insulating materials. However, the thermal conductivity of such a material may be drastically increased if water fills these pores.

The aim of this work is to show the drastic influence of the moisture content on the thermal conductivity and specific heat of porous ceramic materials. The material elected in this study was the most commonly structural material: castables and concrete of Portland cement. Proportioning different grain sizes and types of aggregates, four sets of samples and several porosity levels were obtained. Castables and concrete have several different applications, like to bond, coat, embed, seal and insulate [1–3]. However, the working temperature must not exceed 300°C. In applications were variations on the moisture level and working temperature takes place, the thermal conductivity may have its value doubled, depending on the porosity and moisture level, and temperature of measurement.

In this work it is investigated the effect of adsorbed water, on the thermal conductivity and, specific heat of castables and concrete of Portland cement. The experimental technique employed is the hot wire parallel technique and the measurements were carried out from room temperature up to approximately 300 °C during heating and cooling cycle.

2. Experimental technique

The experimental technique employed in this work is the hot wire technique. It is an absolute, non-steady state and direct method, and therefore it makes use of standards unnecessary. The first practical application of the hot wire technique was reported in 1949 by Van der Held and Van Drunen [4], in the determination of the thermal conductivity of liquids. However it was Haupin [5] who in 1960 first used this method to measure the thermal conductivity of ceramic materials. Nowadays the hot wire method is considered as an effective and accurate means of determining the thermal conductivity of refractories. However, it is not possible to use this method for electrical conductor materials, unless some process of electric insulation between the hot wire and the sample is developed. It is a very suitable technique for the purpose of this work since it is possible to measure thermal conductivities since room temperature, where the presence of water is detected, up to high temperatures. In addition, with the hot wire technique the concept of “mean temperature” between hot and cold face of a sample on thermal conductivity calculations is eliminated, since the measurement is carried out at a fixed temperature. The temperature gradient across the sample is very low, and this is another virtue of this technique, since an ideal method for measuring thermal conductivity would be that one capable of measuring this property across a zero temperature gradient throughout the sample.

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.

This propagation of heat throughout an infinite medium generates a transient field of temperatures, which is logarithmically dependent on time. In practice [6], the theoretical infinite linear source is approached by a thin electric resistance and the infinite solid is replaced by a finite sample.

Four variations of the hot wire method are known [7]. The theoretical model is the same, and the basic difference among these variations lies in the temperature measurement procedure. In this work it was employed the variation known as 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:

$$k = \frac{-q'}{4\pi T(t)} E_{\mathrm{i}}\left(\frac{-\rho c_{\mathrm{p}} r^2}{4kt}\right) \tag{2}$$

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} = especific heat of the material (J/(kg·K)), r = distance between hot wire and termocouple (m), t = elapsed time after begining of heat release (s), $T(t)$ = temperature rise registered by the termocouple related to the initial reference temperature (K), $E_{\mathrm{i}}(-x)$ = exponential integral function.

According to DIN 51046 - Part 2 Standard, the thermal conductivity is determined at several pair of selected t and $2t$ times, by using Equation 2, and the several values obtained are then averaged. In this work a different procedure is proposed. The calculations, starting from the recorded temperature transient in the sample are carried out by using a non-linear least squares fitting method [8]. Both thermal conductivity an specific heat in Equation 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 Equation 1. So, using the same apparatus is possible to determine these three thermal properties in the same experiment.

The apparatus used in this work, as shown in Fig. 1, is fully automatic, and the transient of temperature detected by the termocouple is recorded and processed by a computer via an analog to digital converter using a software specially written for this purpose.

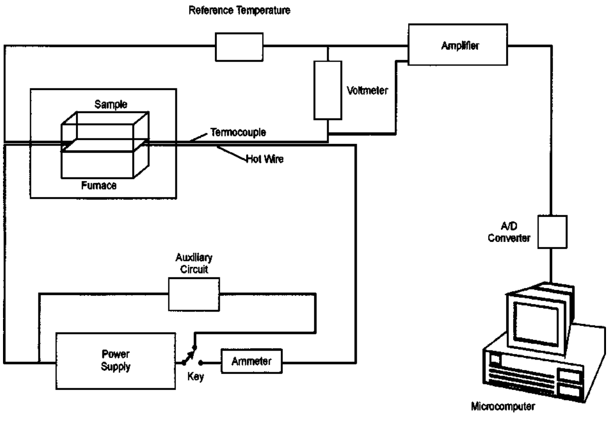


Figure 1 Schematic of hot wire parallel equipment.

3. Sample preparation

The raw material employed were sand, basalt, vermiculite and soda-lime-silica glass, as aggregate and ordinary Portland cement.

The aggregate and cement were then weighed and mixed with the appropriate amount of water to give the desirable consistency. Samples in shape of bricks, having 230 mm × 112 mm × 59 mm were prepared by vibrating the moist mass. A steel mould was employed, and five samples were then cast simultaneously. 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.

Twelve batches of samples, within four sets, denominated by C_1, C_2, C_3 and C_4 according to the type of aggregate employed were prepared using a fixed amount of cement. The moulded samples were then covered with wet cloth and left to stand at room temperature under 75% relative humidity for a period of 24 hours. After this step the samples were demoulded and cured under a 95% relative humidity for 7 days. In the next step the samples were left at room temperature under 75% relative humidity for 21 days, and then they were ready to be tested. Details of the samples are given in Table I.

4. Results and discussions

Measurements were carried out in the temperature range from 20°C up to 300°C, each 50°C during heating and cooling cycle.

Thermal conductivity data obtained are plotted through Figs 2 to 5, and specific heat data are plotted through Figs 6 to 9 as a function of temperature. Heating and cooling cycle are identified by letters H and C.

4.1. Thermal conductivity of green castables

Through Figs 2 to 5, 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 two different regions can be identified in each plot.

TABLE I Sample details

	C_1		C_2		C_3		
Composition (w%)	C_1A_1	C_1A_2	C_2A_1	C_2A_2	C_3A_1	C_3A_2	C_3A_3
Cement	20	20	20	20	20	20	20
Basalt (Stone 1*)	40	40					
Coarse sand*	10	40			78	53	72
Medium sand*	10		80			23	
Fine sand*	10			80			
Too fine sand*	10						
Fine Vermiculite*					2	4	8
Bulk density(Kg/m^3)	2285	2307	1998	2040	1780	1471	1167

	C_4				
Composition (w%)	C_4A_1	C_4A_2	C_4A_3	C_4A_4	C_4A_5
Cement	20	20	20	20	20
Medium sand*	80	60	40	20	0
Ground glass**	0	20	40	60	80
Bulk density(Kg/m^3)	1998	1987	1941	1880	1930

**Particle size distribution from 75μm to 2 mm.

*According to Brazilian standard ABNT NBR 7211/83.

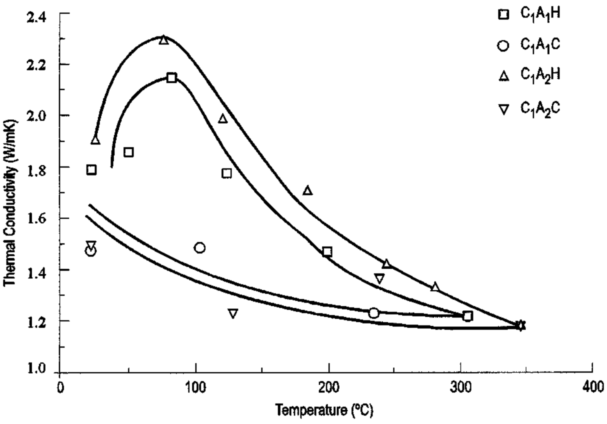


Figure 2 Thermal conductivity as a function of temperature: Set C_1.

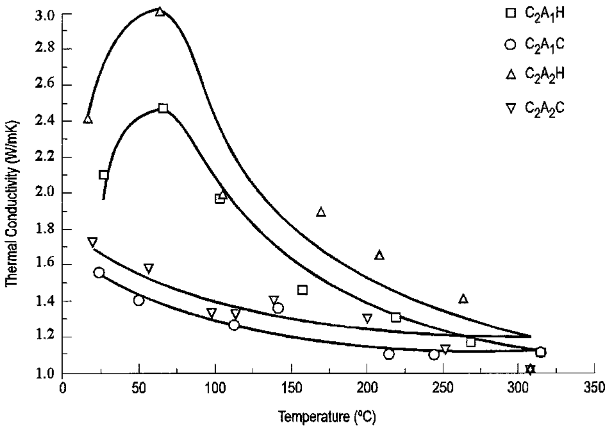


Figure 3 Thermal conductivity as a function of temperature: Set C_2.

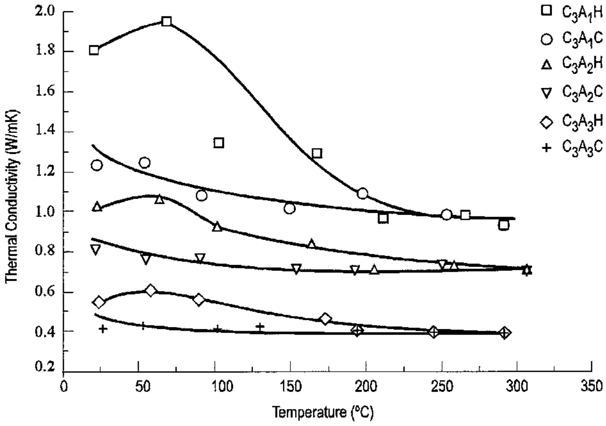
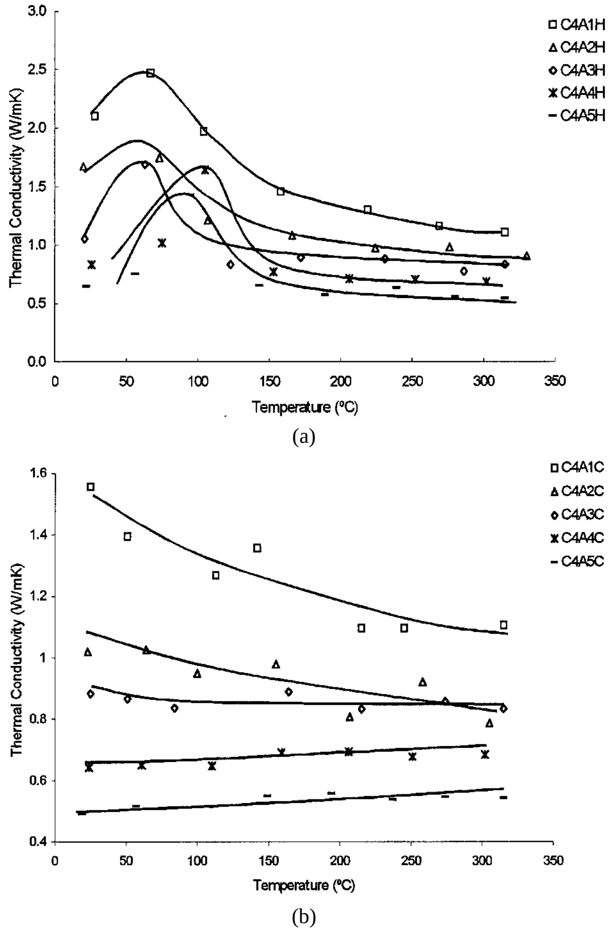


Figure 4 Thermal conductivity as a function of temperature: Set C_3.

Region 1 displays an increase in the thermal conductivity, from room temperature up to approximately 60°C. At this point a maximum is apparentely attained.

Region 2 starts at about 60°C and the thermal conductivity decreases from its maximum value attained at this temperature until its minimum value measured at 300°C.

Similarly to the refractory concrete [9], the trend in region 1 can be explained in terms of the adsorbed water that absorbs part of the heat generated by the electric



(a)

(b)

Figure 5 (a) Thermal conductivity as a function of temperature: Set C_4 (heating), (b) Thermal conductivity as a function of temperature: Set C_4 (cooling).

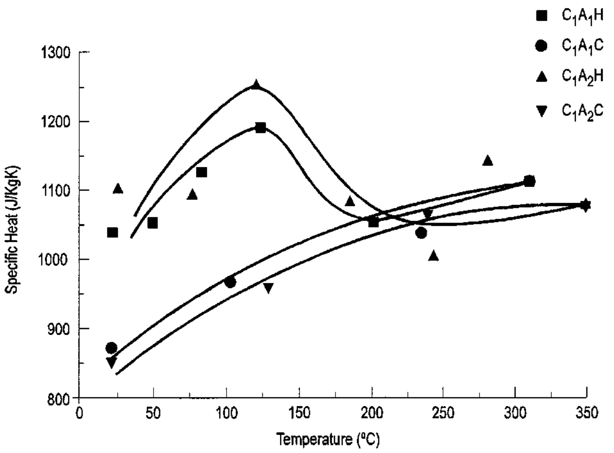


Figure 6 Specific heat as a function of temperature: Set C_1.

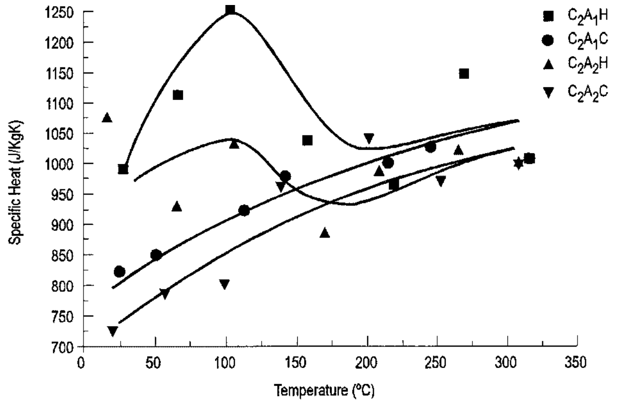


Figure 7 Specific heat as a function of temperature: Set C_2.

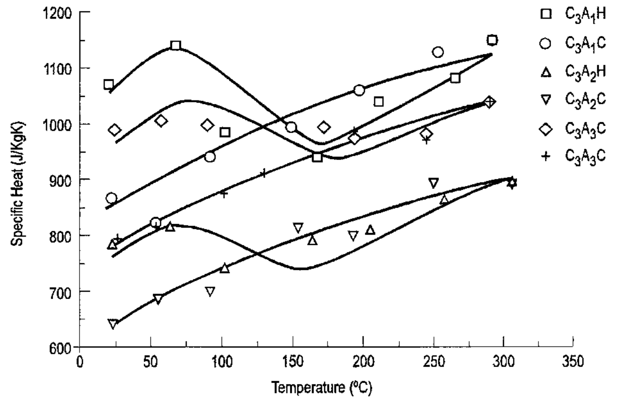


Figure 8 Specific heat as a function of temperature: Set C_3.

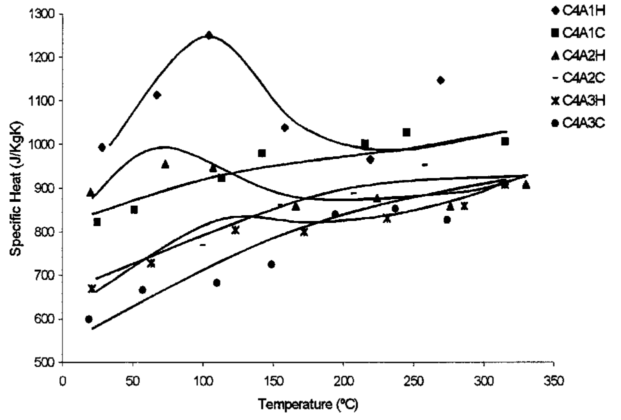


Figure 9 Specific heat as a function of temperature: Set C_4.

current passing through the hot wire. The consequence of this absorption of heat by the water is that the temperature raise at a fixed distance from the hot wire is less than that 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, and this phenomenom explain the values of thermal conductivity measured around 60°C higher than those measured at room temperature. As the temperature increases the amount of adsorbed water decreases (phase transition from liquid to gaseous state occurs around 100 °C), leaving empty spaces behind. The decrease of the amount of adsorbed water and the increase of porosity leads to a decrease in the thermal conductivity.

The combination of these mechanisms of opposite effects, i.e., absorption of energy by adsorbed water and porous formation due to water evaporation leads to a maximum value (around 60 °C), for the thermal conductivity of this porous material as a function of temperature.

Region 2 displays a non-uniform decrease in thermal conductivity. A steep decrease may be observed between 60 °C and 150 °C and can be linked to the loss of crystalization water. This phenomenom readily occurs at 133 °C which was confirmed by DTA. In a second stage, a smooth decrease in thermal conductivity takes place and its minimum value is measured at 300 °C. These mechanisms of porous formation which increase the porosity level between 60 °C and 300 °C explain the decrease of the thermal conductivity in this region.

4.2. Thermal conductivity of dried castables

Heat conduction in dielectric solids may be considered either as the propagation of anharmonic elastic waves through a continuum or as the interaction between quanta of thermal energy called phonons [10]. At high temperatures another mechanism of conduction must be considered: the photon conductivity. However, since this process of conduction is proportional to the fourth power of temperature, it is usually neglected at low temperatures. For a dielectric solid the phonon conductivity is proportional to the specific heat of the material and to the mean free path of the wave:

$$k \alpha c_p \lambda \tag{3}$$

where:
$k =$ phonon conductivity, $c_p =$ specific heat of material, $\lambda =$ mean free path of the wave.

For pure crystalline materials, when temperature increases, specific heat also increases to an approximately 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 [11], the thermal conductivity may be represented by an equation of the form:

$$k = \frac{A}{T} + B \tag{4}$$

where:
$k =$ thermal conductivity, $T =$ absolut temperature, $A, B =$ experimental constants to be determined.

For glasses the mean free path may be considered approximately constant and when temperature increases, thermal conductivity increases in proportion to the specific heat. In this case the thermal conductivity may be represented by an equation of the form [11]:

$$k = CT + D \tag{5}$$

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

If a material is a combination of cristalline and glassy phases [11], the temperature dependence of the thermal conductivity may be represented by the equation:

$$k = \frac{1}{AT + B + \frac{C}{T}} \tag{6}$$

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

The behaviour of the thermal conductivity of the dried material, as shown through Figs 2 to 5 is that one predicted by Equation 6. This material is typically a mixture of crystaline and glassy phases, with predominance of crystaline phases, except for samples C_4A_4 and C_4A_5. Fig. 5b shows that from sample C_4A_3 to C_4A_4 and C_4A_5 there is an inversion of the shape of the curve thermal conductivity versus temperature.

For sample C_4A_4, and C_4A_5, respectively, 60 w% and 80 w% glass was employed as one of the aggregates. The total amount of glassy phase may be still greater, since it is necessary to add the vitreous phase ever present in the material. So, increasing the amount of glass in the composition of the sample, the thermal conductivity versus temperature decreases and an inversion of the slope of the curve is experimentally detected as expected theoretically.

4.3. Specific heat of green castables

Through Figs 6 to 9 it can be seen that there is also a common trend for all samples concerning the temperature dependence of the specific heat. I is also possible to identify two regions in each plot.

Region 1 displays an increase in the specific heat from room temperature up to approximately 100°C. At this point a maximum is apparentely attained, and starting from this point the specific heat decreases with temperature rise and its minimum value is attained at approximately 180 °C (end of region 1). In region 2 (from 180 °C up to 300 °C) the specific heat gradually increases with temperature raise.

The behaviour of the specific heat in region 1 may be also explained in terms of adsorbed water.

The specific heat of a compound material, calculated according to Newmann-Kopp rule is given by:

$$C_p(t) = \sum_{i=1}^{n} F_i C_i(T) \tag{7}$$

where n is the number of phases, F_i is the mass fraction of each phase, and $C_i(T)$ is the corresponding specific heat for each constituent. Specific heat of water is 4 or 5 times the specific heat of fired ceramic materials. So, the specific heat of the compound material is incresead in this region where water is present. As adsorbed and crystalilzation water is eliminated by evaporation with temperature raise, the specific heat decreases from its maximum value at 100 °C, to its minimum value at approximately 180 °C.

In region 2, the specific heat gradually increases with temperature rise and this behaviour is predicted by Debye theory of specific heat [10].

4.4. Specific heat of dried castables

For this kind of analysis, dried castables may be treated like any other ceramic material. The heat capacity increases with the temperature, starting from a low value at low temperatures, and approaching the value $6M$ cal/(mole·K) at high temperatures, where M is the number of atoms per mole. Specific heat is defined as heat capacity per unit mass. This behaviour is predicted by Debye theory of specific heat [10], as shown through Figs 6 to 9.

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