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Thermal conductivity of insulating refractory materials: Comparison of steady-state and transient measurement methods

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ABSTRACT

Measurements of thermal conductivity with the heat flow meter, laser flash method, hot disk method and hot wire method are compared on two kinds of refractory materials: Insulating Boards and Insulating Fireclay Bricks. Heat losses, humidity, anisotropy and heterogeneity can explain the variation in thermal conductivity values obtained with the different techniques. If they are taken into account in the analysis, discrepancy within 10% can be found. The choice of the technique depends on the investigated material and on the level of information required.

1. Introduction

For steel making, the need to reduce heat losses through the lining of steel ladles becomes increasingly important due to the higher energy costs and new laws on environmental impact in industrial situations. The ladle is the vessel to hold and transport the hot liquid steel, in which all the secondary metallurgical operations take place. These operations require large energy input to maintain the liquid steel above the casting temperature. Therefore, the design of the steel ladle lining plays an important role. Many steel manufacturers added an insulation layer between the external steel shell and the safety lining. Its main purposes are: i) reducing heat losses through the lining and ii) keeping the lining in a stable compressed condition [1,2].

Therefore, the selection of an appropriate insulating refractory material becomes crucial. This kind of refractory is usually a highly porous material with low thermal conductivity <1 W m^{-1} K^{-1}. The conductivity may vary with temperature and can evolve with the state of the microstructure [2]. In other words, the initial behaviour characterized at room temperature can differ from that in service conditions. For these reasons, a careful and detailed evaluation of the thermal conductivity is an important aspect for the development and the performance of these materials.

Several methods are used for determining the thermal conductivity of a material. These can be classified into two main categories: steady-state and transient methods. In steady-state methods, the sample is tested after a stable temperature distribution is achieved. The thermal conductivity is obtained by evaluating the one dimensional heat flux due to the temperature gradient across the specimen [3]. The main disadvantage is that this approach requires a long time in order to achieve the equilibrium temperature distribution inside the material. Large sample size and low conductivity increase the time to reach equilibrium. For instance, the samples measured in this work with the heat flow meter needed between 40 and 60 min to reach the equilibrium. On the other hand, individual measurements with transient methods are much quicker, typically less than a minute. In some techniques, such as the hot disk method, it is even possible to evaluate thermal conductivity and thermal diffusivity with a single experiment.

However when different methods are compared, the obtained values can show some variation. Tonnesen et al. [4] compared the hot disk and the laser flash methods on fireclay bricks, chromia/alumina bricks and high alumina bricks. They found a difference between 5% and 20%, depending on the investigated temperature. Bourret et al. [5] compared the heat flow meter and the laser flash method on geomaterial foams

Abbreviations: HFM, heat flow meter; HWM, hot wire method; IB-LD, low density insulating boards; IB-MD, medium density insulting boards; IB-HD, high density insulating boards; IFB, insulating fireclay bricks.

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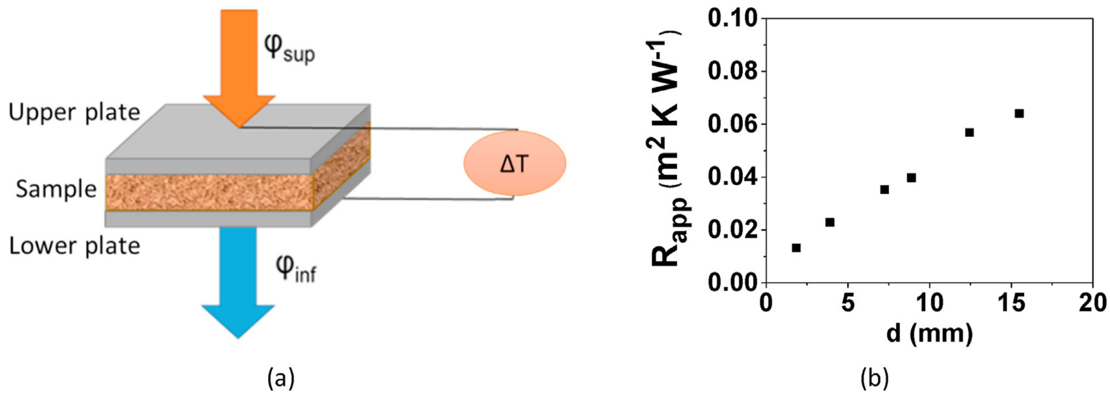

Fig. 1. a) Schematic diagram of the heat flow meter; b) an example of the results obtained with this method for a set of six samples (apparent thermal resistance - R_{app} vs thickness - d).

revealing a maximum discrepancy of 21%. Mathis [6] compared the hot disk and the laser flash methods on homogeneous solid samples with different amounts of conductive alumina filler in a continuous matrix, yielding differences of 20%.

Thus, the discussion about which is the best technique for the refractory field is still open. The main purpose of this paper is to compare four methods: a steady-state method involving a heat flow meter [7] and three transient methods namely the laser flash [8], the hot disk [9] and the hot wire methods [10]. Attention will be focused on the advantages and disadvantages of each of them. The measurements will be made on two kinds of refractory materials: Insulating Boards and Insulating Fireclay Bricks, which both present rather little variation of thermal conductivity with temperature.

2. Materials and methods

2.1. Heat flow meter

The heat flow meter (HFM), supplied by CAPTEC (France), is a steady-state method used to measure the thermal conductivity of insulating materials at ambient temperature [7]. Samples are cut in the form of square slabs with two flat parallel faces and different thicknesses.

The specimen is placed between two thin copper plates equipped with thermocouples and heat flow sensors. An electrical resistance is embedded in the top plate, which acts as a heat source. The power dissipation is chosen in order to impose a temperature difference ΔT of around 4 °C between the upper and lower plates. To improve the thermal contact between the sample and the two plates, a weight is placed on top of the upper plate [5]. A simplified schematic of the measurement is shown in Fig. 1a.

The method measures the apparent thermal resistance R_{app} [m^2 K W^{-1}] using Eq. (1):

$$R_{app} = \frac{\Delta T}{(\phi_{sup} + \phi_{\inf})/2} \tag{1}$$

where ϕ_{sup} is the heat flow supplied to the sample by the upper plate [W m^{-2}], ϕ_{inf} is the heat flow coming out of the sample absorbed by the lower plate [W m^{-2}] and ΔT the temperature difference between the two plates [K]. The apparent thermal resistance is the sum of two contributions: the thermal resistance of the sample R_{th} [m^2 K W^{-1}] and the contact resistance R_c [m^2 K W^{-1}] between the sample and the two plates (Eq. (2)).

$$R_{app} = R_{th} + R_c = d/\lambda + R_c \tag{2}$$

where d is the thickness of the sample [m] and λ the thermal conductivity [W m^{-1} K^{-1}]. Assuming the contact resistance does not vary between specimens, plotting the experimental data as a function of the thickness should yield a linear relation (Fig. 1b). The thermal conductivity is the inverse of the slope and the contact resistance is obtained by the intercept of the linear extrapolation with the y-axis.

In terms of precision, the main factor that affects the values is the thickness. If the samples are too thick, the lateral heat losses will become significant. The overall thermal conductivity increases by up to 8% for the data in Fig. 1b. However, if they are taken into account the accuracy is ±1%. Furthermore, the samples are assumed to have two perfectly parallel faces, but a difference of ±2% is estimated. Thus, the uncertainty of this method at room temperature is taken to be ±3% [7,11].

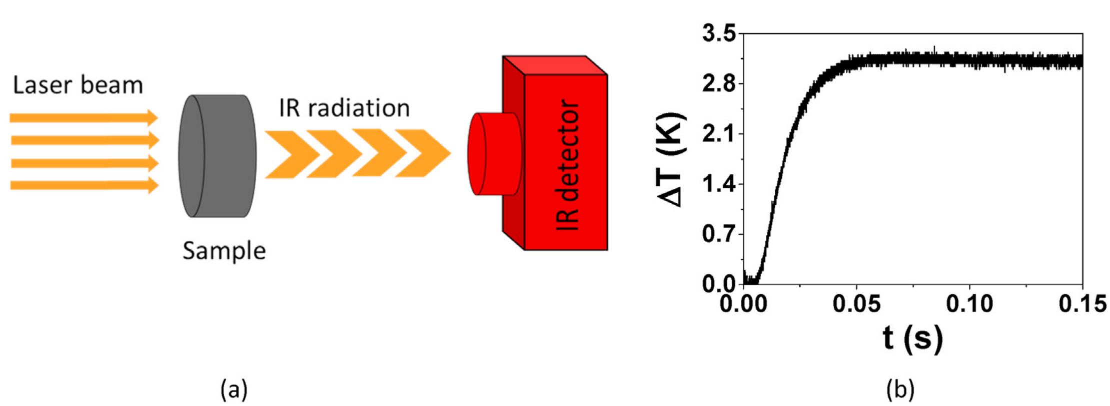

Fig. 2. a) Schematic diagram of the laser flash method; b) evolution of the temperature increase ΔT on the back face as a function of time t.

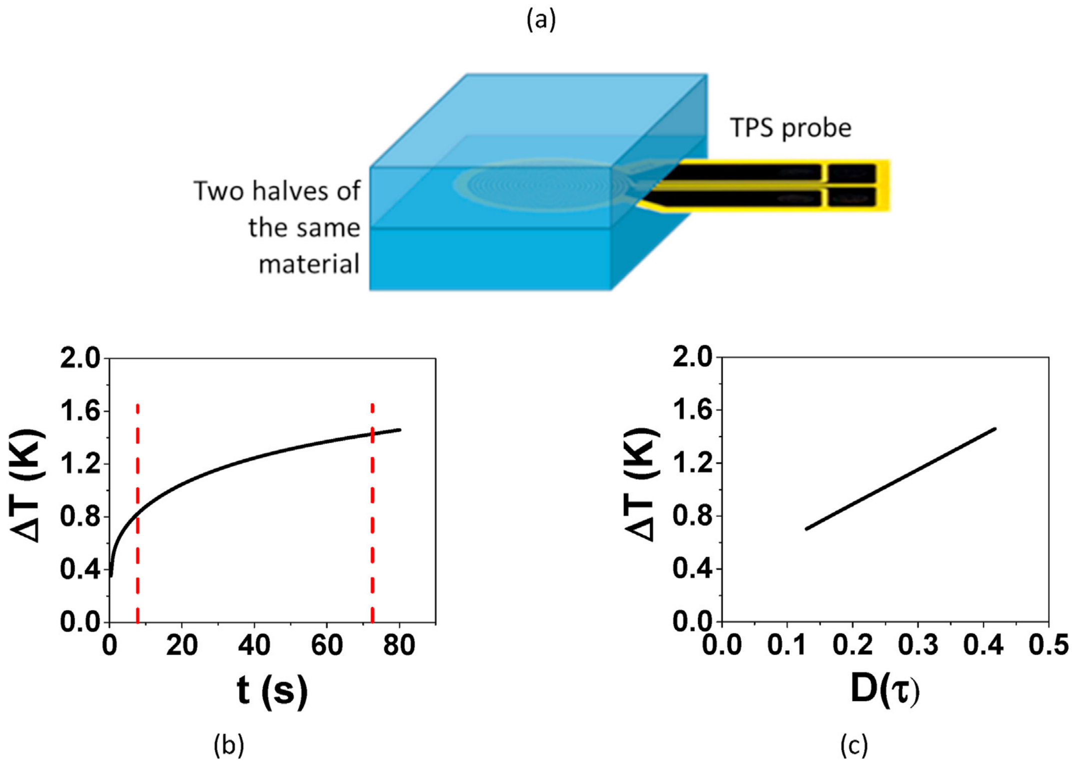

Fig. 3. a) Schematic diagram of the hot disk method; b) increase of the temperature as a function of time; c) linear relationship between the temperature increase and the dimensionless specific time function D(τ). The dotted lines underline the two limit values: t_{min} and t_{max} for the analysis of the thermal conductivity.

2.2. Laser flash method

The laser flash method (LFA) is a transient technique developed by Parker et al. in 1961 for evaluating the thermal diffusivity of different kinds of materials in a short measuring time [8,12]. The main advantages are: i) no contact resistance between the sample and the heat source; ii) easy sample preparation; iii) rapidity of measurements.

The principle consists of sending a light energy pulse to impact on the front face of a disk sample. The temperature inside and outside the sample is assumed to be the same before the pulse and it is measured by a thermocouple, placed close to the specimen. An infrared detector records the increase of temperature on the back face as a function of time (Fig. 2a). A layer of graphite covers the sample. This layer is very important in the case of semi-transparent materials which are typically white in appearance [13]. The purposes of this layer are: i) to increase the heat absorbed on the front face; ii) to increase the radiation emitted by the back face; iii) to keep the absorption constant even if the sample changes colour; iv) to prevent the laser from passing directly through the sample to the detector [13,14]. A simplified schematic of the measurement set up is shown in Fig. 2a.

A typical temperature – time response is presented in Fig. 2b. Assuming that there are no heat losses, the evaluation of the thermal diffusivity from the T-t behaviour can be made using Parker's equation (Eq. (3)) [8]:

$$\alpha = 0.139\frac{d^2}{t_{1/2}} \tag{3}$$

where α is the thermal diffusivity [$m^2\ s^{-1}$], d the thickness of the sample [m] and $t_{1/2}$ the time necessary for the back face to reach half of the maximum temperature [s]. However, the hypothesis of negligible heat losses is not always applicable, especially at high temperatures. For this reason, many other models were developed, for taking into account this effect, such as those of Cape-Lehman [15] and Degiovanni [16]. Furthermore, in the case of semi-transparent materials, another aspect to consider is the direct transmission between the two faces due to radiation effects (e.g. Mehling's model [17]). For these reasons, the analysis of thermal diffusivity in the following paper was made using the Mehling's model for all the investigated temperatures.

The thermal conductivity is, then, calculated using Eq. (4):

$$\lambda = \alpha\rho C_p \tag{4}$$

where λ is the thermal conductivity [$W\ m^{-1}\ K^{-1}$], α the thermal diffusivity [$m^2\ s^{-1}$], ρ the bulk density [$kg\ m^{-3}$] and C_p the specific heat capacity [$J\ kg^{-1}\ K^{-1}$]. For more complex formulations, C_p can be estimated from data for simple components using the rule of mixtures [18].

The measurements were performed using a Netzsch LFA 427 in an argon atmosphere (100 mL min^{-1}). The apparatus is characterized by a vertical setup: the laser system (laser wavelength ~ 1050 nm) is placed at the bottom and connected to the measurement cell by an optical fibre, while the detector (type: InSb) is positioned on the top and cooled by liquid nitrogen.

In terms of precision, the main factors that influence the thermal conductivity results are: i) density (±2%), because the faces might be not perfectly parallel; ii) C_p (±3%), this is affected by the technique used to estimate the chemical composition since it is evaluated with the rule of mixtures; iii) precise knowledge of sample thickness (±0.5%). Thus, the uncertainty in conductivity values for this method is considered to be ±5% at room temperature according to the ASTM report [8]. At high temperatures, the uncertainty in values can increase up to 10–15% depending on the material and on the quality of the T-t curve, which can exhibit noise due to the hot environment and radiation effects.

2.3. Hot disk method

The transient plane source (TPS) technique is also known as the hot disk method or the Gustafsson probe [9,19]. One of the advantages of this technique is the possibility to measure simultaneously the thermal conductivity and the thermal diffusivity, and then to deduce the heat

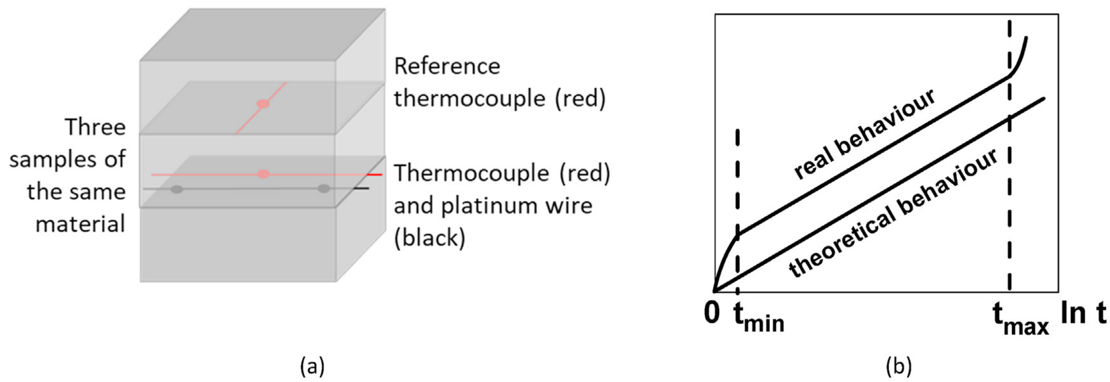

Fig. 4. a) Schematic diagram of the hot wire method; b) difference between the theoretical and the real temperature-time curve.

capacity per unit volume (ρ C_p) [20].

A TPS probe is a double nickel spiral supported by two thin sheets of an insulating material [21,22]. It is placed between two halves of the sample material (Fig. 3a) and has a double function: on one hand, it constitutes the heat source for increasing the temperature of the samples; on the other hand, it works as a "resistance thermometer" for recording the increase of temperature as a function of time (Fig. 3b).

The theory assumes that the probe is placed in a medium of infinite dimensions [21]. To adapt the theory and the reality, two parameters must be chosen: the radius (r) of the probe and the measurement time (t). In the first case, the probe external surface should be restrained to the central part of the samples. In the second case, the chosen measuring time t should guarantee a thermal penetration depth smaller than the real dimensions of the samples in all directions. For this reason, during the analysis of the thermal conductivity, a t_{max} is chosen in order to take into account the finite dimensions of the samples. Furthermore, the mathematical solution assumes a perfect contact between the probe and the two faces in contact. Taking into account the probe-sample contact thermal resistance, some of the initial points recorded (from t = 0 to t_{min}) are removed from the calculation.

The calculation method for evaluating the thermal properties is based on an iteration procedure, which yields the thermal diffusivity (α) as an optimised variable. The result is a linear relation (Fig. 3c) between ΔT(τ) (temperature increase) and D(τ) (dimensionless specific time function) [23,24]. The function D(τ) depends on the geometrical parameters of the nickel spiral and also τ given by Eq. (5):

$$\tau = \sqrt{\frac{\alpha t}{r^2}} \tag{5}$$

where α is the thermal diffusivity [$m^2\ s^{-1}$], t the measurement time [s] and r the radius of the probe [m]. The temperature increase is the sum of two contributions: i) the temperature increase of the sample surfaces facing the TPS probe $\Delta T_s(\tau)$ and ii) the temperature increase which stems from the insulating layers of the nickel spiral, as well as from the contact resistance between the sample and the probe $\Delta T_i(\tau)$. The slope of the linear relation yields the $\Delta T_s(\tau)$ and the intercept with the vertical axis gives the $\Delta T_i(\tau)$ [23].

In the case of isotropic materials, the thermal conductivity is then calculated using Eq. (6) [23,24]:

$$\Delta T_s(\tau) = P_0\left(\pi^{3/2} r \lambda\right)^{-1} D(\tau) \tag{6}$$

where P_0 is the heating power [W], r the radius of the probe [m] and λ the thermal conductivity [$W\ m^{-1}\ K^{-1}$]. The specific heat per unit volume (ρ C_p) is calculated using Eq. (4).

In the case of anisotropic materials, the specific heat per unit volume is an important parameter, which must be used as input data for the analysis software at the beginning of the calculation. If the value inserted is wrong, the ratio between radial and axial results would be false [22]. In this case, the iteration procedure gives the value of radial thermal diffusivity (α_{rad}) corresponding to the plane of the probe (disk). The radial thermal conductivity (λ_{rad}) is then calculated using Eq. (4). Finally, the axial thermal conductivity (λ_{ax}) is calculated using Eq. (7) [23,24]:

$$\Delta T_s(\tau_{rad}) = P_0\left[\pi^{3/2} r (\lambda_{rad}\lambda_{ax})^{1/2}\right]^{-1} D(\tau_{rad}) \tag{7}$$

The measurements were performed both at the Department of Civil Engineering in Coimbra (FCTUC) using a TPS 2500 S and at IRCER using a TPS 1500 in an air atmosphere. At room temperature, two Kapton sensors were used: r = 14.61 mm and r = 6.403 mm.

In terms of precision, the thermal conductivity values depend on the accuracy of the output power, on the radius of the TPS probe and on the time. Furthermore, in the case of anisotropic materials, the values in the two directions strongly depend on the accuracy of the specific heat per unit volume. Thus, the uncertainty of this method is estimated to be around 2–5% for the thermal conductivity and 5–10% for the thermal diffusivity [23].

2.4. *Hot wire method*

The hot wire method (HWM) is a transient method, which is often used for determining the thermal conductivity of refractory bricks. Furthermore, this method has different configurations: the standard technique, which is a cross wire method (the thermocouple is connected to the middle of the wire in the perpendicular direction) [25]; the parallel method [26]; the resistance technique [25]; the two thermocouple technique [25] etc. In this paper, the measurements were made with the hot wire parallel technique with a configuration developed at the Institute of Mineral Engineering (GHI) in Aachen [4]. Three samples are necessary. Between the bottom and the central samples, a thermocouple and a platinum wire are placed in two parallel ground grooves, which are 15 mm apart (Fig. 4a). The reference thermocouple is placed between the central and the top sample in a perpendicular direction compared to the platinum wire (Fig. 4a).

The theory is fairly similar to the hot disk method. The difference is that in this case, the heat source is a platinum wire, which is assumed to be infinitely thin and long and surrounded by an infinite medium [10,27]. When a constant electrical current is applied, a constant amount of heat flux is generated all along the wire and this causes a transient temperature field, which for a given position is logarithmically dependant on time (Fig. 4b). The non-linearity at the beginning of the temperature-time response (from t = 0 to t_{min}) is due to the contact resistance between the samples and the wire, while the non-linearity at the end ($t > t_{max}$) is due to the finite dimensions of the samples [4].

For the parallel method, the thermal conductivity is calculated using Eq. (8) [24,25]:

$$\lambda = -\frac{q}{4\pi T(t)} E_i\left(\frac{-r^2}{4\alpha t}\right) \tag{8}$$

Table 1
Summary of the density and porosity of each investigated insulating refractory material.

Materials	Density (g/cm^3)	Porosity (%)
IB-LD	1.0 ± 7%	55–65
IB-MD	1.2 ± 7%	45–55
IB-HD	1.5 ± 7%	35–55
IFB	0.9 ± 7%	70–75

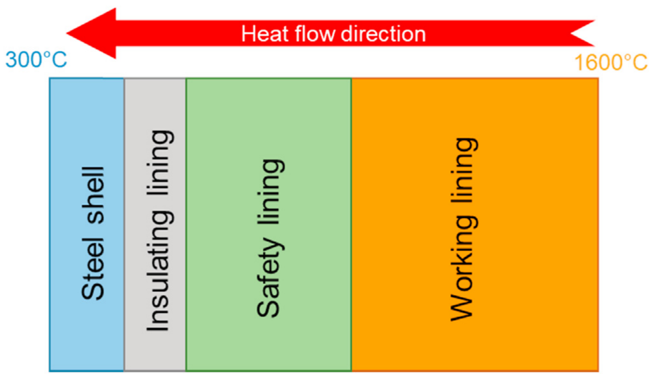

Fig. 5. Schematic representation of a steel ladle lining.

where λ is the thermal conductivity [W m^{-1} K^{-1}], q the heat flow [W m^{-1}], α the thermal diffusivity [m^2 s^{-1}], r the distance between the wire and the thermocouple [m], T(t) the temperature rise compared to the reference temperature [K] and t the time to reach that temperature [s]. E_i is a function given by Eq. (9):

$$-E_i(-x) = \int_x^{\infty} e^{-t} \Big/ t\, dt \tag{9}$$

where $x = \frac{r^2}{4\alpha t}$

The measurements were performed at the Institute of Mineral Engineering (GHI) in Aachen using a Netzsch TCT 426 in an air atmosphere.

The accuracy of the thermal conductivity values is related to: i) nonzero heat capacity of the wire, ii) thermal radiation, iii) outer boundary conditions (axial and radial heat losses), iv) non-constant power dissipation in the Pt wire, v) finite integration time of the voltmeter, vi) temperature drift of the sample surroundings and vii) radius of the wire [28]. Therefore, the uncertainty of this method is taken to be ±6% for small power levels and ±1% for high power levels [28].

Table 2
Sample's dimensions for each method (Φ = diameter, d = thickness, A = area).

Methods	Typical dimensions
Laser flash method	Φ = 10 mm, d = 2 mm
Hot-disk method	A = 70 × 70 mm^2, d = 25–35 mm
Hot-wire method	A = 250 × 114 mm^2, d = 50 mm
Heat flow meter	A = 30 × 30 mm^2, d = 1.5–15 mm

Furthermore, in the case of an anisotropic material, the obtained result represents an average value over different heat flow directions through the sample.

2.5. Materials

Two kinds of refractory materials were studied: Insulating Boards (IB), which are vermiculite-based materials (Fig. 6a), and Insulating Fireclay Bricks (IFB), clay-based materials (Fig. 6b). For the IB, three kinds were analysed: Low Density Insulating Boards (IB-LD), Medium Density Insulating Boards (IB-MD) and High Density Insulating Boards (IB-HD). Table 1 summarizes required physical properties of each material.

The porosity was estimated using the following equation:

$$P(\%) = (1 - \rho_{app} / \rho_r) \cdot 100 \tag{10}$$

where ρ_{app} is the bulk density [kg m^{-3}] and ρ_r the true density [kg m^{-3}] measured using a helium pycnometer. For each material, ten measurements were made. Both investigated refractories are used in the insulating lining (Fig. 5) to reduce heat losses through the wall of the vessel.

Samples of different sizes were prepared for each material, depending on the technique. A summary of the dimensions is shown in Table 2.

An important aspect to underline is the anisotropic behaviour of Insulating Boards due to the layer structure of the vermiculite (Fig. 6a). This implies that the thermal conductivity should be evaluated in at least two directions. For the laser flash method, the samples were prepared so that the cross sectional area was in one case perpendicular to the pressing direction (called “cross-plane” direction) and in the second case parallel to the pressing direction (called “in-plane” direction). For the hot disk method, the anisotropic behaviour was studied using an anisotropic analysis software module, which gives the values of thermal conductivity in the two directions with one measurement. For the hot wire method and the heat flow meter, it was not possible to take into account this aspect. In the first case, the reason is related to the technique itself, which gives an average value of λ. Secondly, for the heat flow meter measurements there was insufficient volume available in the board for extracting samples with the heat flow axis in two different orthogonal directions.

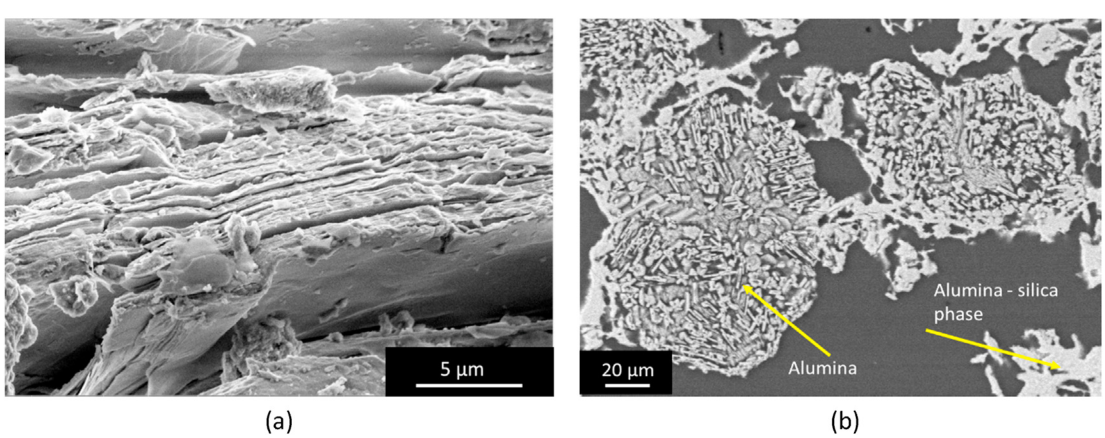

Fig. 6. a) SEM micrograph of Insulating Boards, showing the layer structure of the vermiculite; b) SEM micrograph of Insulating Fireclay Bricks, where it is possible to observe porous alumina grains and denser alumina-silica phases, the darkest phase corresponding to the embedding resin required for the specimen preparation.

Table 3
Thermal conductivity values obtained with the laser flash method (LFA), the hot disk method (TPS) and the heat flow meter (HFM). The refractory materials were measured at room temperature in the "cross-plane" direction.

	LFA λ ($W\ m^{-1}\ K^{-1}$)	TPS λ ($W\ m^{-1}\ K^{-1}$)	*HFM* λ ($W\ m^{-1}\ K^{-1}$)
IB-LD	0.19 ± 1%	0.29 ± 2.6%	0.26 ± 3%
IB-MD	0.22 ± 1.7%	0.35 ± 1.5%	0.36 ± 3%
IB-HD	0.27 ± 1.5%	0.43 ± 1%	0.36 ± 3%
IFB	0.36 ± 3.5%	0.38 ± 3.9%	0.45 ± 3%

On the other hand, the Insulating Fireclay Bricks were considered macroscopically isotropic and thus, only the "cross-plane" direction was analysed. This hypothesis was verified experimentally using the laser flash method on samples cut in two different directions.

3. Results and discussions

The analysis in Table 3 gives the thermal conductivity values for the four refractory materials at room temperature using three techniques: the laser flash method, the hot disk method and the heat flow meter. Room temperature measurements were not made with the hot wire method because the time to achieve the equilibrium temperature distribution inside the material was too long. Only the results for the "cross-plane" direction are shown in the table. This is the most important direction since these kinds of refractory materials are used to reduce heat losses through the lining of the steel ladle.

For the laser flash method, two samples per direction were analysed. For each sample, three measurements were made. In the case of the hot disk method, three pairs of specimens were analysed and for each couple, four measurements were made. Finally, for the heat flow meter, between five and six samples with different thicknesses were measured twice. The percentage value in Table 3 gives the standard deviation, representing the amount of variation in a set of repeated measurements.

Each result is reproducible. The standard deviations are around 3% for the HFM, between 1% and 4% for the TPS and between 1% and 3.5% for the LFA.

It is evident from Table 3 that the three techniques give different values of thermal conductivity, with a maximum discrepancy of around 38%. This value is sufficiently high to merit a more detailed investigation. However, it can be noted that the discrepancy is less for the isotropic material. Several aspects were taken into account in order to better interpret the obtained results.

3.1. Heat losses

Heat losses are an important aspect for both the LFA and the HFM measurements. In the first case, they modify diffusivity values obtained using Parker's relation (Eq. (3)), especially at high temperatures. For this reason, the values were corrected using Mehling's model [17], which has been built into the LFA software. In the case of HFM measurements, it was possible to observe that the heat flow supplied to the sample was greater than the heat flow coming out of the sample. This is due to heat losses by convection on the lateral surfaces, which can be expressed with Newton's law (Eq. (11)):

$$\varphi_{conv} = -Ah(T_{air} - T) \tag{11}$$

where Φ_{conv} is the rate of the heat transfer by convection [W], A the lateral surface area [m^2], T_{air} the temperature of the air [K] and T the temperature of the sample [K]. Furthermore, the difference became larger with the increase of the thickness. These heat losses can be considered as a parallel thermal resistance, which decreases the overall thermal resistance of the material and consequently increases the apparent value of thermal conductivity. A correction was made by introducing heat losses through a heat sink term in the one-dimensional steady-state heat equation (Eq. (12)) [29]:

Table 4
Thermal conductivity values obtained with the heat flow meter, both experimentally (before) and (after) correction taking into account the heat losses.

	HFM λ ($W\ m^{-1}\ K^{-1}$)	
	before	after
IB-LD	0.26 ± 3%	0.24 ± 3%
IB-MD	0.36 ± 3%	0.30 ± 3%
IB-HD	0.36 ± 3%	0.33 ± 3%
IFB	0.45 ± 3%	0.40 ± 3%

$$\frac{d^2T}{dz^2} + \frac{4h(T_{air} - T(z))}{L\lambda} = 0 \tag{12}$$

where h is the heat transfer coefficient [$W\ m^{-2}\ K^{-1}$]. For natural convection in air a value of $h = 15\ W\ K^{-1}\ m^{-2}$ can be used. T_{air} is the temperature of air [K], T(z) the temperature of the material [K], L the length of the sample [m] and λ the thermal conductivity [$W\ m^{-1}\ K^{-1}$] estimated considering only the values for $d < 6$ mm. This thickness value was chosen with the approximation that for small thicknesses, the lateral heat losses are negligible. The corrected values are shown in Table 4.

In the case of IFB, the three methods now give rather close results. The discrepancy is within 10%. In the case of IB, the difference between the heat flow meter and the other two methods in the "cross-plane" direction is now around 26%. A similar discrepancy was found by Bourret et al. on geomaterial foams comparing the HFM and the LFA [5]. This means that some other aspects should be taken into account.

3.2. Humidity

Porous solids in humid atmospheres exhibit higher overall thermal conductivity. This is explained by replacing the air in the pores with a thermal conductivity of 0.026 $W\ m^{-1}\ K^{-1}$ [30] by water with a thermal conductivity equal to 0.6 $W\ m^{-1}\ K^{-1}$ [31]. Work on humidity effects and drying suggests that this water is located as a film layer on the inside of the pore surface [32,33]. This can help to understand why the LFA gives the lowest values of thermal conductivity.

The LFA measurements were made in an argon atmosphere. To be sure, that inside the furnace there was only Ar, the samples were first subjected to three cycles of vacuum followed by filling with argon. As a consequence, the samples were effectively dried before the measurements. On the other hand, the TPS and the HFM were measured in the air atmosphere of standard laboratory conditions, with a typical humidity of 50%. In fact, the nature of the Insulating Boards containing layered vermiculite grains makes these IB samples particularly sensitive to their thermal and hydric history.

However, to verify the influence of the presence of the humidity, one pair of samples for each IB was left 24 h in the oven at 200 °C, cooled down up to room temperature in a desiccator and then measured again. This temperature was chosen in order to remove the physically adsorbed

Table 5
Thermal conductivity measurements on Insulating Boards and Insulating Fireclay Bricks before and after drying in the "cross-plane" direction. The measurements were made with the hot disk method. The table also shows the water content on the dry basis.

	TPS λ ($W\ m^{-1}\ K^{-1}$)		*W (%)*
	before	after	
IB-LD	0.29 ± 2.6%	0.23 ± 2.6%	4–5% wt.
IB-MD	0.35 ± 1.5%	0.28 ± 1.5%	4–5% wt.
IB-HD	0.43 ± 1%	0.34 ± 1%	4–5% wt.
IFB	0.38 ± 3.9%	0.38 ± 3.9%	<0.05% wt.

Table 6
Thermal conductivity values obtained with the heat flow meter (HFM), the hot disk method (TPS) and the laser flash method (LFA) at room temperature in the "cross-plane" direction after considering the effects of heat losses and humidity. HFM values have been adjusted considering equivalent "dry" conditions of the LFA and TPS results.

	LFA λ (W m^{-1} K^{-1})	TPS λ (W m^{-1} K^{-1})	*HFM* λ (W m^{-1} K^{-1})
IB-LD	0.19 ± 1%	0.23 ± 2.6%	0.18 ± 3%
IB-MD	0.22 ± 1.7%	0.28 ± 1.5%	0.22 ± 3%
IB-HD	0.27 ± 1.5%	0.34 ± 1%	0.26 ± 3%
IFB	0.36 ± 3.5%	0.38 ± 3.9%	0.40 ± 3%

water and the water molecules residing in the particle spaces of the vermiculite [34,35]. The same temperature was also used in the case of IFB to have comparable experimental conditions. For each material, the water content (W) on the dry basis was estimated using the following equation [36]:

$$W(\%) = \left(\frac{m_i - m_f}{m_f}\right) \cdot 100 \tag{13}$$

where m_i is the mass of the sample before drying [kg] and m_f the mass of the sample after drying [kg]. The results of this simple experiment are shown in Table 5.

The table shows two behaviours. The isotropic IFB material seems to not be affected by the humidity. Thermo-gravimetric analysis (TGA) on IFB showed no loss in mass up to 1000 °C, which is also confirmed by the estimation of the water content (<0.05% wt.). In the case of the anisotropic materials, by removing 4–5% wt. of water, the thermal conductivity decreases by around 25%. Therefore, drying is an important step to avoid overestimating λ.

The same correction was made on the results obtained with the heat flow meter. The values have been adjusted to equivalent "dry" conditions of the LFA and TPS trials. Table 6 summarizes the values obtained with the three methods at room temperature taking into account the effects of the heat losses and the humidity.

It is possible to observe that the values obtained with the HFM and the LFA are now rather close, even in the case of the anisotropic materials. The maximum discrepancy is within 10%. In contrast, the TPS method gives higher thermal conductivity values in the case of the anisotropic materials with a maximum discrepancy of around 26%. It is important to underline that the three methods do not correspond to exactly the same experimental conditions. For instance, the LFA and the HFM involve similar heat flow directions (linear in both cases), while for the TPS, the heat flow is spherically radial from the disc shape probe. Furthermore, the hot disk method uses larger sample dimensions, yielding a better average value of thermal conductivity in the case of heterogeneous materials.

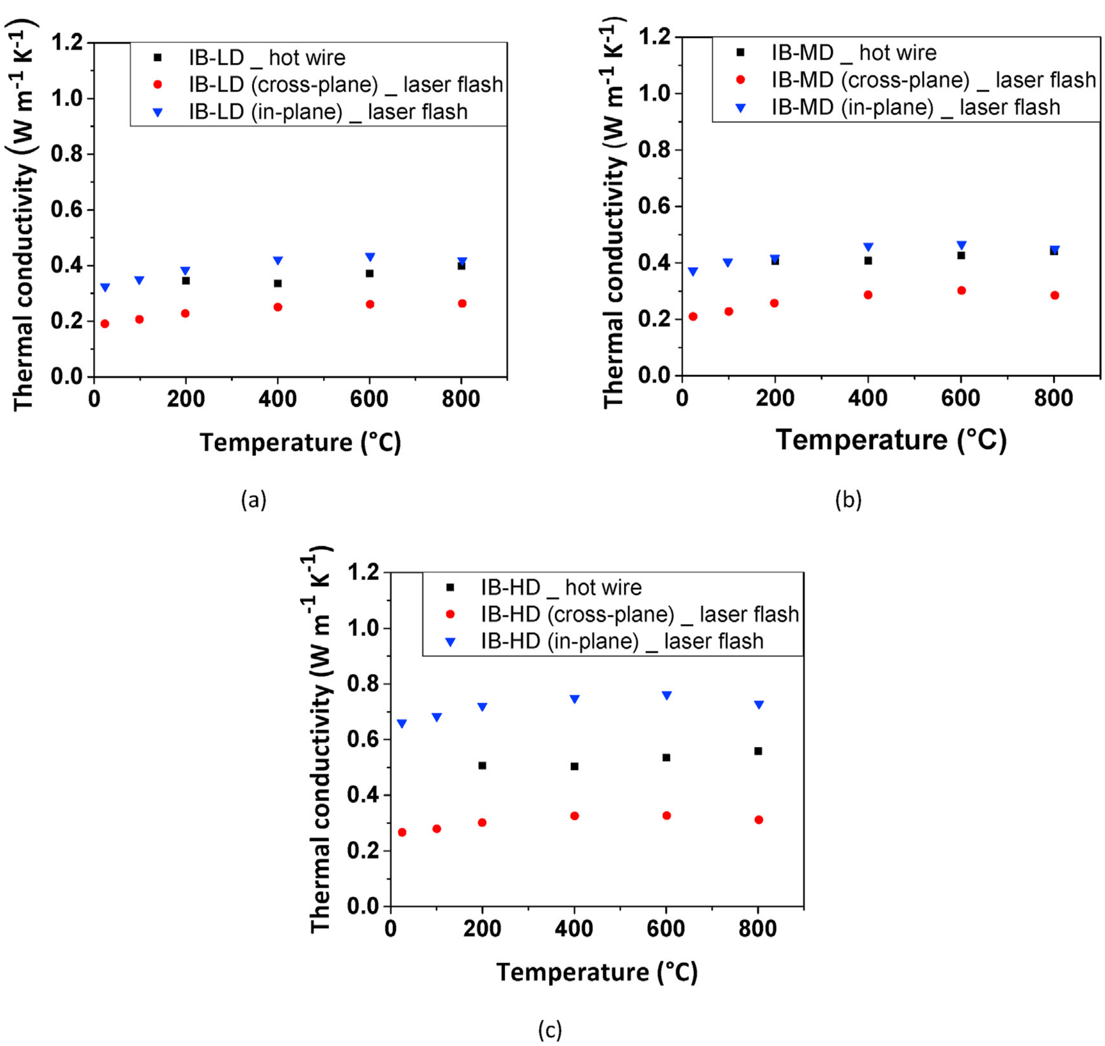

Fig. 7. Comparison between the hot wire and the laser flash methods on Insulating Boards (Low Density (a), Medium Density (b) and High Density (c)).

Table 7
Summary of the main advantages and disadvantages of each investigated technique.

Method	Measured parameter	Range[a]	Uncertainty[a]	Sample shape	Sample dimensions	Heat source	Anisotropy	Heat losses	Heterogeneity
LFA	α	0.1–1000 mm^2 s^{-1}	±5%	Cylindrical	Φ: 10 mm d: 2 mm	Light energy	2 values - 2 samples	Model correction	–
TPS	λ α	0.005–500 W m^{-1} K^{-1}	2–5% 5–10%	Square/ cylindrical	70 × 70 × 25-35 mm^3	Electrical resistance	2 values - 1 measurement	–	More precise average value
HWM	λ	<15 W m^{-1} K^{-1}	1–6%	Square	250 × 114 × 50 mm^3	Electrical resistance	Average value	–	More precise average value
HFM	λ	<1 W m^{-1} K^{-1}	±3%	Square	30 × 30 × 1.5–16 mm^3	Electrical resistance	2 values - 2 samples[b]	Model correction	–

[a] ASTM and ISO standards.
[b] It is possible to determine the anisotropic behaviour of a material, if sufficient volume of the material is available to cut samples in different directions.

3.3. Heterogeneity and anisotropy

The Insulating Fireclay Bricks have a fine microstructure which, at the macroscale, is homogeneously distributed (Fig. 6b). This means that small mm sized samples can be representative of the entire brick. This interpretation is also confirmed by the results shown in Table 6, in which the maximum discrepancy between the three techniques is within 10%.

On the other hand, the Insulating Boards have microstructures with greater heterogeneity, mostly linked to the layer structure of the vermiculite and its orientation (Fig. 6a). After the correction of the effects of the heat losses and the humidity, the difference between the HFM and the LFA is within 10%, while the difference between the TPS and the other two methods is within 26%. This might be related to the effect of the heterogeneous microstructure.

The effect of heterogeneity is linked to the anisotropic conductivity of individual grains. Furthermore, orientation of these grains in brick forming leads to anisotropic thermal conductivity at the macroscopic scale. If this factor is not taken into account, the input value in the modelling studies of the heat transfer through the lining of steel ladles will be higher than the real value and thus, the thickness of the insulation to apply will be overestimated with economic consequences.

To verify this interpretation, hot wire measurements were made on IB samples (Fig. 7). The results are compared to those obtained with the LFA method in the two directions. The graphs for the three refractory materials show that the thermal conductivity values given by the HWM are between those obtained with the LFA. In particular, they are higher than the values obtained in the "cross-plane" direction, which is the most important direction. This supports the interpretation of a slight overestimation of the thickness of the insulation layer based on HWM values.

Furthermore, Fig. 7 also shows that with the reduction of the pore volume fraction the effect of the anisotropy becomes more significant. High Density Insulating Boards (Fig. 7c) exhibit a higher difference between the λ values in the two directions compare to Low Density (Fig. 7a) and Medium Density (Fig. 7b) Insulating Boards. This validates the hypothesis that the anisotropic behaviour is related to the orientation of the layer structure of the vermiculite. The higher proportion of solid phase in the IB-HD emphasizes this characteristic compared to the homogenizing effect of the isotropic pores.

4. Conclusion

Thermal conductivity is an input parameter, which is required for modelling of heat transfer through a steel ladle lining. Therefore, its estimation is of primary importance. Several methods can be used to evaluate the thermal conductivity, but each of them can give a different value. Differences can be explained by considering parameters such as:

- Heat losses: it can increase the apparent value of thermal conductivity by 5–10%;
- Humidity: it can increase the thermal conductivity by 15–25% in a porous material;
- Heterogeneity and anisotropy: it can vary the thermal conductivity by 10–15%.

For each method, the effects of these factors were analysed and where needed, corrections were made to the obtained values. Table 7 summarizes the main advantages and disadvantages of each technique.

Therefore, the answer to the question, which is the best technique, is linked to the type of material investigated and to the level of information required.

If the analysis is made on a homogenous isotropic material, the methods give rather close results. Discrepancy may be within 10% if heat losses and humidity effects are taken into account. On the other hand, for heterogeneous materials, the hot disk and the hot wire methods give more accurate values due to the larger dimensions of the samples. However, if the material is anisotropic, the hot wire method provides less detailed information in the form of an average value over the radial direction to the hot wire axis.

Another important aspect to consider is the time: transient methods are faster than steady-state methods and this time increases with the decrease of the thermal conductivity.

Considering all these aspects, in the present paper the best technique seems to be the hot disk method, both for the Insulating Boards and the Insulating Fireclay Bricks.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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