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Note

Measurement of the thermal conductivity of clays used in pelotherapy by the multi-current hot-wire technique

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ABSTRACT

We measured, using the multi-current hot-wire method, the thermal conductivity (λ) of two different clay pastes suitable to be used as peloids. The same wire and system was used to measure the λ of water, and the results were compared with literature data. Special attention was paid to statistical data analysis. The obtained λ values for the clay pastes are higher than the λ of water at the same temperature.

1. Introduction

The word *peloid* (from the ancient Greek *pelos*, or ash-colored) refers to different kinds of sediments whose composition include principally silicates (micas, clays feldspars,…) but also carbonates, sulphates and different amounts of organic substances. When mixed with different quantities of sea water, spring waters or medicinal waters, these minerals form pastes that have been used since ancient times as therapeutic agents (mud baths). *Pelotherapy* refers to the use of peloids as therapeutic or wellness agents, principally but not only, at spas and thermal centers. There exist excellent updated reviews in the specialized literature about the therapeutic and/or wellness use of muds, peats and clays and for further details we refer, for instance, to Viseras et al. (2007). In many traditional thermal centers peloids were obtained from the local neighborhood. However, nowadays an increasing number of spas are obtaining their peloids by mixing with local water powder clays mined elsewhere and supplied by specialized companies.

During last years a number of scientific studies on the thermo-physical properties of peloids have been carried out (Cara et al., 2000; Beer et al., 2003; Legido et al., 2007), but still a systematic characterization is needed. In this note we present experimental measurements of the thermal conductivity (λ) at temperatures near 40 °C of two different pastes, suitable to be used as peloids, prepared from clays mined in Spain.

2. Materials and mineralogy

We studied pastes based on two different clays, namely, magnesium bentonite (BEMG) and sabhasana (SABA). They were obtained from the suppliers as powder, and mixed with different amounts of distilled water in our laboratory to prepare the pastes. The BEMG sample was obtained from a quarry in Magán (Toledo, Spain), where is mined for industrial purposes (mainly sewage filtering), it has a greenish color and a very small particle size (88% of particles smaller than 20 μm). The SABA clay was obtained from another quarry in Málaga (Spain), where is mined mainly for use in the cosmetics industry, it has a greyish color. The two clays selected for this study have a very small particle size, which is one of the properties determining their suitability for use in mud baths at spas.

Both bulk and clay mineralogical composition of the clay powders used in the present study were studied in detail by Legido et al. (2007), using X-ray diffraction and other techniques. Therefore, we just briefly summarize here the results presented earlier. The acronyms (BEMG, SABA) used to distinguish among the different clays are adopted from Legido et al. (2007).

The bulk mineralogy study of the BEMG showed a high content of phyllosilicate (94%). The presence of other minerals was very low and limited to traces of quartz, calcite and feldspars. Regarding the clay mineralogy, the sample is composed mainly of smectite (95%). Consequently our BEMG sample can be considered as a monomineral clay. Chemical analysis showed that, besides silica, the most common compound was magnesium oxide. For this reason we refer to this sample as magnesium bentonite.

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The bulk mineralogy study of the SABA clay showed a phyllosilicate content of 52%, plus 18% of quartz, 15% of calcite, 11% of dolomite and traces of other minerals. Regarding the clay mineralogy, this sample has a mixture of smectite (41%), illite (38%) and kaolinite (21%). Consequently SABA sample cannot be considered as mono-mineral clay and it is better classified as a common clay.

The water content for each clay was the following: the BEMG sample with a 60% (w/w) of water and the SABA sample with a 40% (w/w) of water. Quantities of powder clay and of water were weighted with a digital balance (±0.01 g), and mixed in a beaker maintained at 40 °C, the temperature at which measurements were later done. Strong stirring was applied to the mixture by a mechanical stirrer, until an homogeneous paste is formed.

3. Experimental

The transient hot-wire technique is nowadays accepted as the most precise and reliable method to measure the thermal conductivity of fluids, over a wide range of temperatures and pressures. For the best experiments, the uncertainty of the results is estimated to be ±0.5% (Nagasaka and Nagashima, 1981; Assael et al., 1987).

The experimental setup and method employed in this investigation are essentially the same recently used in our laboratory for the measurement of the thermal conductivity of several fluids (Khayet and Ortiz de Zárate, 2005; Vázquez Peñas et al., 2008). Hence, only a brief description is given here and we refer the reader to Vázquez Peñas et al. (2008) for details.

The core of the experimental setup was a platinum wire of 50 µm diameter and approximately 21 cm of length. A Keithley 2400 source-meter, which can act simultaneously as current source and voltage meter, was employed for the electrical measurements. This instrument was interfaced to a personal computer and a software code was written to retrieve the measurement points, fit the data, and calculate the thermal conductivity.

Thermal conductivity measurements of paste clays were performed with the wire in a horizontal configuration. For this purpose, a measurement cell was build in stainless steel. It consisted of a rectangular double-wall recipient of 28 cm length and 7 cm width. Water from a thermostated bath at about 40 °C was circulated through the jacket of the measurement recipient. Sample preparation was performed by first casting a clay layer (thickness about 1 cm) over the thermostated bed, using a spatula to attain a very flat surface. Then, the wire mounted over a flat frame was placed over the surface of this first clay layer. A second clay layer, of approximatively the same thickness as the first, was then carefully cast, covering completely the wire with its supporting frame. The second layer was then covered with an impervious film, to reduce water evaporation. Finally, a platinum resistance thermometer was inserted inside the sample. This thermometer was also interfaced to the computer controlling the experiment. Temperature values reported in this note were those measured with this thermometer, that stabilized at about ±1 °C around the 40 °C programmed in the thermostats.

When an electrical current I was circulated through the wire, because of Joule heating, the wire temperature increased. The rate of wire heating depends on the thermal conductivity and on the thermal diffusivity of the sample surrounding the wire (Carslaw and Jaeger, 1959). As temperature increases, so does the electrical resistance of the wire R and the voltage drop between the wire ends V. For an infinite straight wire, solving the heat equation in cylindrical coordinates, it can be shown that the voltage difference between two points, for large times, increases logarithmically (Kestin and Wakeham, 1978).

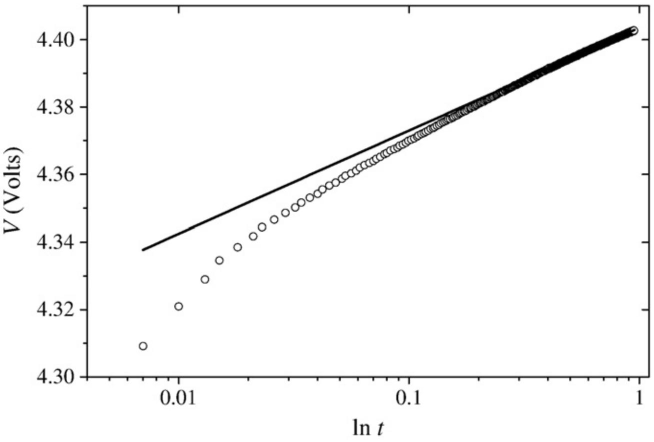

Fig. 1. Typical individual heating curve: voltage drop in the wire, V, as a function of time, t, when using the peloid clay magnesium bentonite at 38.9 °C and 340 mA.

A typical heating run lasted for a couple of seconds during which 350 measurements were acquired. As an example, we show in Fig. 1, on a semi-logaritmic scale, the voltage drop in the wire (V) as a function of time for a heating run with magnesium bentonite (60% w/w water content) at a temperature of 38.9 °C, and using a current $I = 340$ mA. For each heating run, the thermal conductivity of the sample was obtained by fitting the data pairs $\{\Delta V_i, ln(t_i)\}$ to a straight line, from which a slope b was derived. Only the points acquired after ≈213 ms were actually used in the fitting procedure. The solid line in Fig. 1 represents the logarithmic fit of the long-time experimental points. Some deviations at short times are obvious, which can be ascribed to not having reached yet the asymptotic long-time behavior, as well as to finite-size of the wire and other systematic effects. From the slope b the thermal conductivity is obtained as (Khayet and Ortiz de Zárate, 2005; Vázquez Peñas et al., 2008):

$$\lambda = \frac{mI^3R_0}{4\pi L b}, \tag{1}$$

where R_0 is the electrical resistance of the wire at the beginning of the heating run, L the length of the wire, and $m = \alpha R_0$ the slope of the $\{R - T\}$ curve at the initial temperature, α being the temperature resistance coefficient of the wire material. For this work we performed heating runs using different values of the current, scanning I from 260 mA to 360 mA in steps of 20 mA. This scanning procedure is referred to as multi-current hot-wire, and itgives more reliable values of λ as further discussed below.

Initially, the method allows for an absolute determination of the thermal conductivity using known values of m and L. The uncertainty of the λ values obtained in this way is mainly determined by the validity of the theory, all unaccounted factors contributing as systematic errors and limiting the uncertainty of the absolute measurements to a few percent (Khayet and Ortiz de Zárate, 2005). An alternative approach that gives more accurate λ values was described and successfully used by Vázquez Peñas et al. (2008). It consist in performing relative measurements, *i.e*, to rewrite Eq. (1) as:

$$\lambda = A\frac{I^3R_0}{b}, \tag{2}$$

where A is a "calibration" constant that is assumed to be independent of the sample under test, or the temperature. A calibration fluid whose thermal conductivity is known can be used to infer a value for A. If measurements are performed at various temperatures or with various calibrating fluids, a better estimation of the calibration constant can be obtained. Once A is determined, its value is used to evaluate the thermal conductivity of the samples under test. Initially, the calibration parameter A includes the length of the wire and the slope m of the $\{R, T\}$ curve, but it also represents all unknown sources of systematic errors.

To calibrate the wire we performed runs with water at two different temperatures (namely, 20 °C and 40 °C) with the same cell and setup used for the paste clays. In particular, the wire was in a horizontal position. Heating curves like that plotted in Fig. 1 were carefully examined, and no convection was detected for long times. Series of calibration runs were performed at the beginning and at the end of the experiments, as well as when switching between the clays. For each calibration series and each temperature, we computed an average $<I^3R_0/b>$ (with its corresponding uncertainty) by the method described in Sec. 3.1. We determined the calibration constant by comparison with known values of λ(T) for water, including the recommendations of ASTM-D2717 and other literature sources (Assael et al., 1989; Bohne et al., 1984). From such a comparison we found

$$A = 0.0169\ \text{W}\ \text{m}^{-1}\text{K}^{-1}\text{A}^{-2}. \tag{3}$$

There exists a ≈4% deviation between the adopted A value, Eq. (3), and the one determined form the α of Platinum and the measured length of the wire. We interpret this difference as a probe of the various systematic errors included in the experimentation.

The calibration procedure is shown graphically in Fig. 2. Filled circles with error bars represent, for each temperature and calibration series, the obtained thermal conductivity of water adopting the A value of Eq. (3). Error bars represent 1-σ confidence intervals, obtained from the gaussian fittings discussed in Sec. 3.1. Star symbols represent the reference λ(T) values. With the adopted A value we reproduced the known λ(T) data within the uncertainty intended in our measurements. Furthermore, we found no significative differences between calibration runs performed at the beginning, at the end, and when switching between tested clays. This demonstrates the stability of the setup throughout the whole period of measurement.

3.1. Statistics

For this investigation we have performed a large number of individual heating runs, such as the one illustrated in Fig. 1. For instance, for the calibration with water, at each temperature, we have performed at least 250 individual heating runs. For the clay pastes, the number of individual runs was lower, around 100 in each case. We set a waiting time of 3 min between individual runs, to allow the system to go back to equilibrium.

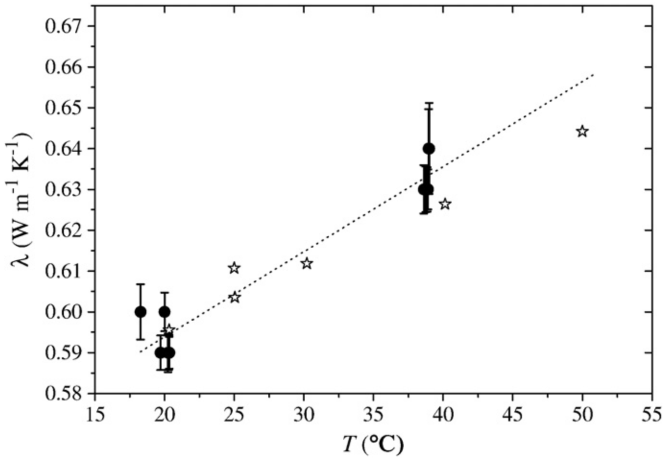

Fig. 2. Calibration with water at two temperatures. Filled circles with error bars are our calibration measurements, performed at the beginning and at the end of the experiments, and also when switching between different clays. Stars represent ASTM-D2717 recommendations and other literature data (Assael et al., 1989; Bohne et al., 1984). The straight line is just a guide to the eye.

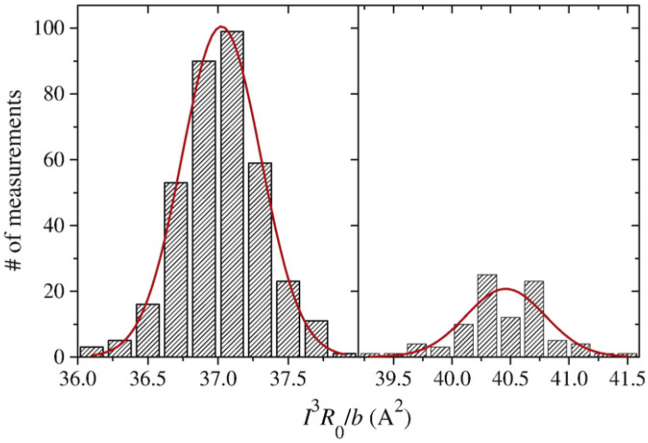

Fig. 3. Histogram of experimental results obtained in the calibration run with water after the SABA test (left), and in the BEMG test (right). Solid curves represent (non-normalized) gaussian fittings.

The large number of individual runs allowed us to perform detailed statistics. As an example, we show in Fig. 3 histograms of the distribution of I^3R_0/b values (binned at 0.2 A^2 intervals), obtained from the calibration series with water at 40 °C after the SABA test (left panel), and from the BEMG test (right panel). In these cases, 360 individual heating runs were performed for water and 96 for the BEMG sample. Superimposed to the histograms in Fig. 3 we show fits to (non-normalized) gaussians. It is worth recalling that Fig. 3 includes I^3R_0/b values obtained at six different current intensities between 260 mA and 360 mA. The fact that the measured I^3R_0/b values spread around a common value, irrespective of the applied current, confirms the adequacy of data analysis via Eq. (2) and enhances the reliability of the λ values. Furthermore, the distribution of data obtained for the clay pastes was well explained by single gaussians, hence, our samples may be regarded as homogeneous and water evaporation can be neglected, at least within the uncertainty of our measurements.

All the thermal conductivity values reported in this note were obtained by the analysis depicted in Fig. 3. Hence, for each calibration or measurement series, histograms of the distribution of experimental I^3R_0/b values obtained from individual heating runs were fitted to gaussians. From the water histograms, we determined the calibration constant A. The λ of the clay pastes were obtained from the corresponding histograms, using the A value determined from the water series. In these cases, reported mean values and errors were obtained from the gaussian fitting, thus, representing ±σ confidence intervals.

3.2. Thermal conductivity of the clay pastes

In Table 1 we summarize the measured thermal conductivity values for the two studied clay pastes. As a reference, we report in the second column of Table 1 the density of the pastes, measured at 22°C with a pycnometer (accuracy 1%) using toluene as reference fluid. In

Table 1
Density, ρ (at 22 °C), and thermal conductivity, **λ** (at indicated temperature T), for the two peloids investigated. For the thermal conductivity, quoted uncertainty accounts only for random errors and corresponds to 1-σ confidence intervals. Uncertainty of density measurements is 1%.

Peloid	Water content (w/w)	ρ (g cm^{-3})	T (°C)	λ (W m^{-1} K^{-1})
Magnesium bentonite (BEMG)	60%	1.27	38.9 ± 0.6	0.68 ± 0.06
Sabhasana (SABA)	40%	1.56	41.4 ± 0.2	0.82 ± 0.13

the third column we report the temperatures at which thermal conductivity measurements were performed, obtained as average and standard deviation of the platinum resistance thermometer readings.

The λ values reported in the fourth column of Table 1 were obtained by the histogram-gaussian fitting method of Sec. 3.1, multiplying the average $<I^3R_0/b>$ by the calibration constant A of Eq. (3). The reported errors are the variances obtained from the gaussian fittings, representing around 9% for the SABA sample and up to 16% for the BEMG sample. No error was considered for the calibration constant A. As discussed above, A had some systematic error that we estimated as about ±4%, and that, initially, should be add in quadrature to the error values reported in the table.

4. Discussion and conclusions

By using the A value reported in Eq. (3) we can convert the calibration series into values for the thermal conductivity of water, as already done in Fig. 2. Averaging the five water series performed at 40 °C, we obtain a mean "measured" thermal conductivity as: $\lambda_w = 0.63 \pm 0.01\ \mathrm{W\,m^{-1}\,K^{-1}}$, that agrees well with reported literature data (Assael et al., 1989; Bohne et al., 1984). A comparison with the clay paste values reported in Table 1 shows that the two pastes have thermal conductivity larger than water at the same temperature. Furthermore, the clay paste with the higher water content (BEMG) has the lower λ, while the paste with the lower water content (SABA) has the higher λ.

The thermal conductivity of bentonites, with smectite content similar to what we found for our BEMG sample, has been thoughtfully studied recently (Beziat et al., 1988; Villar et al., 2006; Tang et al., 2008), mainly because their possible use as buffer materials in nuclear waste disposal. Unfortunately, the water content of the bentonite samples used in these investigations is much lower than in our case. Because of the low water content, these bentonites have a porous structure and the air trapped into the pores is an important factor affecting their thermal properties. To account for this trapped air effect these samples are often compacted by a press to a given density before performing λ measurements (Beziat et al., 1988; Villar et al., 2006; Tang et al., 2008). In our case, with high water content, trapped air was not an issue and our pastes were homogeneous (see Sec. 3.1). Therefore, a detailed comparison of these results with our present data is not feasible.

A similar situation occurs with the many experimental data and theoretical models that exist for the thermal conductivity of soils in general, and of clay soils in particular, with agricultural or environmental aims. See, for instance, the classical study of de Vries (1963) or the more recent papers by Abu-Hamdeh and Reeder (2000) or Abuel-Naga et al. (2008). These studies refer to clays with water content much lower than the one considered in this note, and with non-negligible porosity so that trapped air is an important factor affecting their λ. Again, because of the high water content our pastes were homogeneous and a comparison of our present data with soil thermal conductivities is not feasible.

More relevant are thermal properties investigations of actual peloids (Cara et al., 2000; Beer et al., 2003; Legido et al., 2007). However, most of these authors report only the cooling rates of particular samples. The cooling rate has to be considered a derived property, and it is precisely our final goal to predict cooling rates from more fundamental properties like thermal conductivity, heat capacity or density. Very few authors reported λ data of peloids (Beer et al., 2003) and in those cases they quoted values lower than that of water, what is a quite surprising result.

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